NATIONAL IMPLEMENTATION PLAN FOR THE STOCKHOLM CONVENTION DEVELOPMENT IN MOLDOVA

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The Stockholm Convention foresees the protection of the human health and the environment from persistent organic pollutants. The Stockholm Convention has been ratified by the Republic Moldova on February 19, 2004 and entered into force at the international level on Mai 19, 2004. Elaboration of the strategies and the national implementation plans is one of the requirements stipulated by the Stockholm Convention.

The National Strategy on the reduction and elimination of POPs and National Implementation Plan of the Stockholm Convention (NIP), have been approved by the Government decision nr.1155 on October 20, 2004. These documents insure the implementation of the Stockholm Convention and contribute in the solving of the environmental problems regarding the POPs impact on the human health and environment.

The National Implementation Plan was developed within a participatory process including public participation with assistance from the World Bank and the Global Environment Facility (GEF) in the period of 2002 – 2004. Relevant ministries, departments, NGOs and local public authorities were involved. The process was based on an initial inventory, legal and institutional assessments, objectives and priority setting, NGOs consultation. The document was developed with the participation of the national and international experts.

Background

Over the last 40 years the awareness has been growing globally about the threats posed to human health and the environment by the ever-increasing emissions and discharges into the natural environment of various toxic and hazardous substances. Mounting evidence of health and environmental damage has focused the attention of the international community on a category of substances referred to as Persistent Organic Pollutants (POPs.) Some of these are used as pesticides, while others are industrial chemicals. They are also generated unintentionally as byproducts of combustion and industrial processes. POPs possess *toxic characteristics, are persistent, accumulate in the fatty tissues of most living organisms, are prone to long-range transboundary transport and are likely to cause significant adverse human health or environmental effects near to and distant from their sources*. The realization of POPs' health and environmental threats led a number of countries to introduce policies and legislation to manage an increasing number of these chemicals. Due to POPs' persistence and propensity to cross-border movement, states are also seeking multinational cooperation to address the challenge.

The 1995 Global Programme of Action for the Protection of Marine Environment from Land-based Activities and the 1998 POPs Protocol to the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP) were responses to this serious situation. The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was one of the first to address management of toxics, complemented later primarily by the Rotterdam Convention on the Prior Informed Consent (PIC) Procedure for Certain Hazardous Chemicals and Pesticides in International Trade. In addition, it was acknowledged that there was sufficient scientific evidence for immediate international action regarding 12 POPs. The Convention on Persistent Organic Pollutants (The Stockholm or POPs Convention) was adopted and opened for signature at the Conference of Plenipotentiaries in Stockholm on May 22, 2001. The Convention will become legally binding on May 19, 2004.

The overall objective of the Stockholm Convention is to protect human health and the environment from POPs[1]. It makes specific reference to the precautionary principle as set forth in Principle 15 of the Rio Declaration on Environment and Development. The Stockholm Convention provides subscribing Parties with basic objectives, principles and elements to be used in developing comprehensive programs and control regimes with respect to POPs. It is structured to address POPs that are a) *intentionally produced*, such as pesticides

[1] The 12 chemicals listed in the Convention are: aldrin, chlordane, dieldrin, endrin, heptachlor, mirex, toxaphene, DDT, hexachlorobenzene, PCBs, chlorinated dioxins and chlorinated furans.

and PCBs, and b) *produced* and *released unintentionally* as the result of human activity, including dioxins, furans, PCBs, and HCB. The nine chemicals currently listed in **Annex A** of the Convention are subject to a ban on production and use except where there are generic or specific exemptions. In addition, production and use of DDT, a pesticide still used in many developing countries for malaria and other diseases vector control, is severely restricted, as set forth in **Annex B** of the Convention. Import and export of the ten intentionally produced POPs is allowed only for the purpose of environmentally sound disposal under restricted conditions.

Special provisions are included in the Stockholm Convention for those Parties with regulatory assessment schemes to review existing chemicals for POPs characteristics and to take regulatory measures with the aim of preventing the development, production and marketing of new substances with POPs characteristics.

Releases of unintentionally produced by-products listed in **Annex C** are subject to continuous minimization with, as objective, the ultimate elimination where feasible. The most stringent control provision with regard to by-products is that Parties shall promote and, in accordance with their action plans, require the use of best available techniques (BAT) for new sources within major source categories.

The Convention also foresees identification and safe management of stockpiles containing or consisting of POPs. Waste containing, consisting of or contaminated with POPs should be disposed of in such a way that the POP content is destroyed or irreversibly transformed so that it does not exhibit POPs characteristics. Where this does not represent the environmentally preferable option or where the POPs content is low, waste shall be otherwise disposed of in an environmentally sound manner. Disposal operations that may lead to recovery or re-use of POPs are explicitly prohibited. With regard to shipment of wastes, relevant international rules, standards and guidelines, such as stipulated in the Basel Convention, are to be taken into account.

The POPs Convention requires the Parties to develop implementation plans to indicate how they will meet their obligations under the Convention. The implementation plans are to be transmitted to the Conference of the Parties within two years of the Convention entering into force. In addition, the Convention sets forth a number of obligations that the Parties shall or which they are encouraged to undertake, including designating a national focal point, fostering information exchange, providing technical assistance, promoting and facilitating public awareness and participation, consultation and education, stimulating research and monitoring, and reporting "at periodic intervals." The Republic of Moldova signed the Stockholm Convention on May 23, 2001 and ratified it on February 19, 2004.

Moldova has severe public health and environmental problems linked to the intensive pesticides use in the past. The stockpiles of obsolete (including POPs) pesticides are a continuous threat to the health of thousands of people. The country has accumulated large amounts of PCB oils and PCB-contaminated equipment in the energy sector presenting high risks to the environment and public health. At the same time, Moldova lacks credible evidence about the current releases, the degree of environmental contamination and health impacts due to unintentionally produced POPs and PCBs. The Government of Moldova acknowledges that elimination of POPs will serve the long-term interests of public health, the environment, and economic development of the country.

In 2001, the Government of Moldova reaquested from the Global Environment Facility (GEF) financial assistance for strengthening its capacity to fulfill the obligations arising from the POPs Convention, including the development of a planning framework to identify priority activities. This assistance has been provided in the framework of a $410,000 GEF POPs grant – "Enabling activities related to the implementation of the Stockholm Convention on POPs in the Republic of Moldova". The National Implementation Plan (NIP) is one of the main outputs of this project. The goal of the NIP is to provide a framework and management options and measures in order to meet the obligations taken by Moldova by joining the Stockholm Convention and to reach the national objectives and priorities regarding the POPs.

The Ministry of Ecology, Construction and Territorial Development[2] (MECTD) assumed the main responsibility for developing the NIP as the state authority responsible for compliance and enforcement of national legal requirements and international obligations related to management of toxic and hazardous products and substances. It must be stressed that the NIP was developed as an interagency and cross-sectoral

[2] The MECTD was recently reorganized into the Ministry of Ecology and Natural Resources. The previous name will be used throughout this document.

document. The National Implementation Plan was prepared by a multi-disciplinary group of national experts. From the very beginning, the NIP development was approached as a process with active participation of all stakeholders and based on the shared responsibility of the governmental bodies, local communities, consumer groups, the business sector, scientific community, NGOs, etc.

A preliminary national inventory of POPs was undertaken in order to provide quantitative information for initiating development of an Action Plan. Gathered data allowed for setting priorities and determining the national objectives in the field of POPs minimization and elimination, a process in which national stakeholders were largely involved. On the basis of the discussed and agreed priorities and objectives the National Implementation Plan was formulated for different areas of POPs. Small problem-oriented teams were set out, to tackle specific issues related, for example, to persistent organic pesticides or PCBs or POPs monitoring and research. During their activity, members of the teams worked closely with counterparts in the appropriate governmental or non-governmental sectors. Workshops were organized that brought together senior representatives of all of these sectors in order to discuss national strategies and options for eliminating POPs.

The NIP includes both regulatory and non-regulatory measures targeting POPs. It is obvious that POPs are only a small part of the chemicals that need control and monitoring in view of their possible impact on the environment and human health. Therefore, POPs issues are treated in the NIP as an independent chemical management issue only to the extent this is related to the direct fulfillment of specific obligations arising from the Stockholm Convention. In all other relations, POPs activities have to be integrated in the overall strategy to protect human health and the environment from the risks resulting from exposure to toxic substances.

In the same time, the NIP is consistent with the national sustainable development strategy and programs aiming at harmonizing economic, environmental and social aspects of development. The Economic Growth and Poverty Reduction Strategy, currently prepared by the Government, will determine the country development in the medium term. In the context of the NIP, poverty and environment are related through a complex web of relationships. Environmental conditions have major effects on the health, opportunity, and security of poor people. A large part of the Moldovan population is actively involved in or directly depends on agriculture activities, which makes them susceptible to impacts from obsolete pesticides. Contamination of agriculture land and foodstuffs with POPs pesticides residues compromises the future options for developing organic agriculture and undermines the export potential of agriculture products. Therefore the sound management of POPs has not to be treated as an exclusively environmental issue. One of the major themes of the NIP is that improving environmental conditions by mitigating POPs-related problems can help to stimulate economic growth and reduce poverty. The many links between environmental management and poverty reduction provide the rationale for systematic mainstreaming this nexus in the NIP priority activities.

The NIP is structured as follows. Chapter 2 provides a very brief profile of the country including general social, economic, environmental and environment management information. Chapter 3 introduces the principles of the NIP development. An assessment of POPs-related issues in Moldova is presented in Chapter 4. The political statement and country strategy in the field of POPs and chemical management are presented in Chapter 5 and the actions incorporated in the NIP follow in Chapter 6. Finally, Chapter 7 provides the framework for implementation, evaluation and updating of the NIP. More detailed background information can be found in the NIP Background Paper and technical reports which are provided on the project website[3].

NIP principles and development

The philosophy that guided NIP preparation was based on the understanding that the control and elimination of POPs has to be integrated into the broader context of *sound chemicals management*. The most efficient improvement in POPs could be achieved in close connection with the fulfillment of other national needs and international obligations in this field.

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[3] See <www.moldovapops.md>

means the *establishment of environmentally sound and integrated management of chemicals*, the *institutionalization of precautionary principle* and *integrated pollution and prevention control* in particular sectors. POPs monitoring has to be integrated in the national environmental monitoring system; reporting on POPs has to be part of the general environmental reporting procedure; public information, awareness and education has to encompass, besides POPs, other chemicals.

It follows from the above that POPs NIP can serve as a triggering policy instrument for developing national programs for sound chemicals management. The general principles underlying the NIP preparation are:

- *Integration in the national development and environmental policy*. The NIP is not a stand-alone document. It was developed as a part of the national environmental policy (NIP POPs actions are combined with other environmental actions) and it is consistent with the national sustainable development strategy. The integration of POPs activities in the overall Moldova environmental policy is one of the *conditions sine qua non* to achieve needed efficiency and to contribute to the improving of the environmental situation in general.
- *Integration of chemical management issues in other sectoral policies*. POPs management is not to be treated as an exclusively environmental issue. The NIP is a national document, adopted by the Government, where the obligations of all stakeholders are clearly defined. One of the major themes of the NIP is that improving environmental conditions by mitigating POPs-related problems can help to stimulate economic growth and reduce poverty. The problem of POPs has to be directly related to the economic activities also as a new business opportunity. Sound management of pesticides can help the agricultural sector[4] to promote Moldova's organic agriculture products worldwide. In this sense, introduction of POPs issues in national agriculture policy could bring direct benefits to this sector. Likewise, the energy sector can benefit from PCBs elimination by reducing occupational health impacts, introducing PCB-free and modern energy saving equipment and optimization of infrastructure.
- *Partnership and shared responsibility*. Setting up realistic objectives and effectively reaching them is possible only within a partnership of all beneficiaries (e.g. consumers, the general public) and stakeholders – the business sector, national and local authorities, local communities, NGOs, and the international community. A wide range of interests in chemical management exist and a broad base of involvement and support is required. Each part should assume its share of responsibility. Involvement of different stakeholders in the project preparation was also needed to estimate the national technical capabilities for solving POPs problems[5]. Agriculture and energy sectors are the most important stakeholders which have to be directly involved in solving most of existing problems with obsolete pesticides and PCBs.
- *Coordination with relevant national policy documents and strategies* (e.g. Economic Growth and Poverty Reduction Strategy, National Environmental Action Plan, National Program for Production and Domestic Wastes Management, Concept of Environmental Policy of the Republic of Moldova, National Environmental Health Action Plan, National Program of Environmental Safety, and Concept of National Water Policy).
- *Coordination with and building on international experience* - relation to other Conventions (Rotterdam, Basel) and relevant international documents. Regional co-operation frameworks (e.g. Transnational Monitoring Network under the International Commission for the Protection of the Danube River) will be used to resolve the POPs issues in Moldova.
- *Emphasize pollution prevention and low-cost solutions*. Remediation of POPs impacts is very costly. Prevention of their releases into the environment through adequate management systems is likely to bring benefits through saving efforts and money. In preventing future and remediating existing damages Moldova will seek to develop affordable low-cost solutions.
- *Right to know and prior informed consent principles*. These establish the basis for ensuring that mechanisms exist for end-users, the public and particularly all potentially impacted individuals have access to information about chemicals and the impacts they may have, and that use is undertaken in that knowledge.

[4] Agriculture is the most important economic sector in Moldova and the biggest employer. Introduction of organic farming practices may be the key to resolving the problems in agriculture on a sustainable basis and would increase the income of individual farmers. Convincing the international community that POPs and other chemicals are under control would increase the export opportunities for Moldovan organic agriculture products.

[5] Significant resources will be necessary to solve the problems of e.g. obsolete stockpiles or PCBs. To find low-cost solutions a close cooperation with the national business community and research institutions will be needed.

- *Use measurable indicators and assess performance*. The NIP has to be subject to revisions and updating on regular basis. This obviously will be linked to the performance evaluation process. The NIP will include a set of verifiable indicators which will provide for doing that.

The elaboration of the NIP followed the stepwise approach as described in the UNEP/World Bank "Guidance for Developing a NIP for the Stockholm Convention" dated October 2003. A preliminary inventory of POPs in Moldova was undertaken in order to provide quantitative information for initiating development of an Action Plan. The inventory provided a better understanding of the situation which allowed for setting priorities and determining the national objectives in the field of POPs minimization and elimination, a process in which national stakeholders were largely involved. On the basis of the discussed and agreed priorities and objectives the NIP was formulated for different areas of POPs. Small problem-oriented teams were set out, to tackle specific issues related, for example, to persistent organic pesticides or PCBs or POPs monitoring and research. During their activity, members of the teams worked closely with counterparts in the appropriate governmental or non-governmental sectors and businesses. Workshops were organized that brought together senior representatives of all of these sectors in order to discuss national strategies and options for eliminating POPs.

Action plan

The goal of the NIP is to ensure compliance with the national obligations under the Stockholm Convention and to reduce and eliminate risks to human health, the environment and national development from past, current and future exposure to POPs. The NIP seeks to encourage, facilitate and support, to the extent possible, national and local authorities in their efforts to collect and properly dispose POPs as well as to remediate or contain sources of POPs pollution.

Moldova has developed this NIP and intends to use the full range of tools to prevent, reduce and eliminate releases and stockpiles of 12 POPs. These tools include international, regulatory, programmatic, voluntary, remedial, compliance monitoring and assistance, enforcement, and research tools. GRM will continuously analyze POPs pollutant sources and reduction options as bases for grouping pollutants, activities, and sectors to maximize efficiencies in achieving reductions. GRM will coordinate integration and sequence actions within and across national action plans, and will seek to leverage these actions on international and industry-sector bases.

NIP priority setting

The determination of NIP priorities included the following steps: defining the process and methodology, selecting the ranking criteria, consulting NGOs and stakeholders, validating identified priorities, and transferring priority areas to the NIP objectives. A wide spectrum of stakeholders participated in discussions on which problems are most critical and what measures would be most appropriate for implementation of Stockholm Convention and NIP development.

The following groups of criteria were selected to be used for ranking POPs priorities: (i) direct benefits to the public and environmental health as well as economic and social benefits; (ii) magnitude of the problem at different levels (international, national, local); (iii) perception by different stakeholders (international community, central and local governments, NGO and the general public, businesses); and (iv) affordability & availability (technology, infrastructure, staff, financial perspective). The list of Stockholm Convention requirements was assessed against selected criteria and five priority areas and respective NIP objectives, important for Moldova in a short-term perspective, were identified:

Manage stockpiles (pesticides and PCBs) and wastes (all chemicals under Convention) in a safe, efficient and environmentally sound manner in order to reduce or eliminate releases.

- To improve legal and regulatory framework for management of obsolete pesticides, supported by development and introducing of management guidelines and practices.
- To foresee incentives for rural communities showing the best results in managing pesticide stockpiles.
- To clearly delimitate responsibilities of all stakeholders for enforcement of legal requirements.
- To propose low-cost urgent measures for reduction of releases at the existing stockpiles (pesticides and PCBs), to re-assess and improve national capacities for safe collection, transportation and storage of obsolete pesticides and implement re-packaging and centralisation followed by the safe disposal of obsolete pesticides.

Develop and implement strategy for identification of POPs-containing stockpiles, wastes and products/articles

- To improve POPs pesticides stockpiles and wastes inventory in respect of risk assessment issues.
- To improve PCBs stockpiles and wastes inventory in respect of clear identification of PCBs content and hot-spot identification.

Develop strategy for identifying and remediation of contaminated sites

- To strengthen national capacities for environmental monitoring and research of POPs content in the natural surroundings (soil, water, living organisms).
- To develop guidelines for contaminated site identification, including rapid assessment of sites, environmental risk identification, sampling and analytical methodologies.
- To implement a pilot identification of contaminated sites, test identification guidelines, and, if successful, create conditions for country-wide replication.
- To assess feasibility, local acceptability and affordability of remediation options.

Promote and facilitate public information, awareness, education

- To ensure public information, develop specific education and awareness programs, set up mechanisms for public participation, maintain training efforts, involve industry and users, establish adequate information dissemination mechanisms.

Encourage/undertake research, development and monitoring

- To prepare realistic and needs oriented research, development and monitoring programs.
- To improve institutional framework and technical capacity for monitoring the POPs and monitor priority sources/major releases.
- To monitor release reduction as an indicator of NIP implementation.

The NIP will focus on short-term and urgent measures while other Stockholm Convention requirements will be considered in a medium- and longer-term perspective after evaluation of implementation results and updating the document.

Given the financial constraints, favourable environmental living conditions in the country should be achieved by implementing actions that will bring maximum social, economic and environmental benefits for the given levels of expenditures. Considering this criterion**,** the NIP gives the highest priority to measures that mitigate the direct negative impacts on environmental health and human well being. The NIP primarily focuses on most affordable, low-cost activities, associated with actions for creation of sustainability, public involvement and at the interest of the international community and government.

Severe economic and financial constraints limit the country's capability to achieve expected level of POPs release reduction. Therefore, one of the country's first priorities is commitment of sufficient international financial resources, specifically for technical assistance and for resolving urgent problems posing significant threats to public health and the environment. Thus, an important focus of developing a policy framework should be finding new means and schemes for resource mobilisation and the financing of environmental expenditures as well as addressing to other barriers for NIP implementation (lack of incentives for resource saving and environmental improvements related to macroeconomic difficulties, weak environmental regulations and enforcement, the insufficient technical capacity of public institutions, deficiencies in information sharing and disclosure, and public outreach).

The intention of this NIP is to make the whole of the GRM's efforts on POPs pollutants more than the sum of its parts. NIP will derive from stronger multi-media coordination among national and sectoral programs, and through the significant involvement of stakeholders. Creation of institutional structure(s) capable to sustain such an approach is a clear current priority.

Proposed actions

The NIP foresees a number of measures to be undertaken in the short-term, presented in the table below. A more detailed description is provided in Annexes 1-4. The proposed actions can be grouped in 4 categories, as follows:

Legal, Regulatory and Institutional Activities

These actions are targeted at amending the current legislation specifically related to the Stockholm Convention and incorporating provisions for establishing a broader chemical safety approach in the country. They also include drafting of specific regulatory acts and supporting operational guidelines and practical handbooks. An important element is creation of adequate institutional arrangements for co-ordination of POPs related activities country-wide and dissemination of experience gained for overall chemical safety aspects.

Capacity Building

This category includes actions related to training of professionals and decision makers, improvement of POPs inventories, increasing the capabilities for hot-spots identification, reporting, monitoring and control, research and development.

On-ground Remediation Measures

These include repackaging and centralisation of obsolete pesticides at the district storage facilities, identification of most appropriated solution for their final elimination, low-cost measures to minimise impacts from abandoned storage facilities, collecting old DDT stocks from the rural households, and remediation measures at the pesticide dump in Cismichioi and the stockpiles of out-of-use capacitors in Vulcanesti and other places.

Public Awareness, Training and Education

The measures responding to the most urgent needs refer to raising public awareness and ensure proper communication on POPs-related issues, and incorporation of POPs issues in educational programmes.

NATIONAL IMPLEMENTATION PLAN FOR THE STOCKHOLM CONVENTION ON PERSISTENT ORGANIC POLLUTANTS IN THE REPUBLIC OF MOLDOVA

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The Republic of Moldova signed the Stockholm Convention on May 23, 2001 during Conference of Plenipotentiaries on the Stockholm Convention on Persistent Organic Pollutants, which was held in Stockholm (Sweden). As signatory to the adopted Stockholm Convention, the Republic of Moldova was eligible immediate country for Global Environmental Facility (GEF) financial assistance to develop a National Implementation Plan in conformity with stipulations of the article 7 of the Convention. In 2001, the Government of Moldova requested from the Global Environment Facility (GEF) financial assistance in strengthening its capacity to fulfill the obligations arising from the POPs Convention, including the development of a planning framework to identify priority activities. As a result of country efforts the National Implementation Plan (NIP) has been developed in the framework of the GEF Project "Enabling activities related to the implementation of the Stockholm Convention on POPs in the Republic of Moldova". Simultaneously, the Ministry of Ecology and Natural Resources as Party to some multilateral environmental agreements (MEAs), regulated POPs, has elaborated the National Strategy on the reduction and elimination of Persistent Organic Pollutants (POPs).

NIP Legal Status, Duration and Coordination

The National Strategy on the reduction and elimination of t Persistent Organic Pollutants (POPs) and National Implementation Plan for the Stockholm Convention on POPs was approved on 20 October 2004 by the Decision No. 1155 of the Government of the Republic of Moldova.

The above-mentioned National Strategy and NIP for the Stockholm Convention on POPs include a large number of inter institutional activities focused on solving the POP issues in the Republic of Moldova ensuring that the impact of POPs on human health and the environment is reduced. The strategy envisages some short-term actions to be implemented during 2004 and 2009 and twelve long-term actions. The National Implementation Plan (NIP) provides a policy framework and describes concrete interventions to reach the national objectives and priorities regarding the management of Persistent Organic Pollutants (POPs), and to meet the obligations taken by the Republic of Moldova under the Stockholm Convention. The NIP seeks to encourage, facilitate and support national and local authorities in their efforts to collect and properly dispose of POPs as well as to remediate or contain sources of POPs pollution.

The Ministry of Ecology and Natural Resources (MENR) is the central national environmental authority which has been designated the Stockholm Convention competent authority by the Law on Ratification of the Stockholm Convention on Persistent Organic Pollutants, No. 40-XV from 19.02.2004.

Also, by Article 4 of the Government's Decision No. 1155 from 20 October 2004, the Ministry of Ecology and Natural Resources has been designated as responsible for coordinating the realization of the provisions of the National Strategy on reduction and elimination of the Persistent Organic Pollutants and National Implementation Plan for the Stockholm Convention on POPs .

Other Involved Institutions

In accordance with Strategy and NIP provisions, the following central public authorities are involved in implementation of POP related activities and realization of these chemicals management issues: Ministry of Health, Ministry of Agriculture and Food Industry, Ministry of Industry and Infrastructure, Ministry of Defense, Department of Standardization and Metrology, and the Department for Emergency Situations of the Ministry of Internal Affairs, Ministry of Education and Youth, Customs Service and National Bureau of Statistics. Other stakeholders are National Academy of Sciences, Regional Environmental Center – Moldova, economical agents, nongovernmental organizations etc. Local authorities have responsibilities for environmental protection against POPs and POPs management in the limits of their territory.

Existing Legal and Regulatory Framework for NIP Implementation

Main legislation

Based on *Constitution of the Republic of Moldova*, which declares that each person has a right for the ecologically safe environment, the laws governing the implementation of the national policies and their implementation being the most relevant ones toward the chemicals, including POPs, control in Moldova are as follows:

- *Law on Regime for Hazardous Products and Substances* (1997) is the main legal act related to chemicals, including pesticides, management. It lays down the distribution of competences between the different ministries and agencies and regulates the management, production, storage, transport, handling, reporting, disposal, import and exports of dangerous chemicals in order to avoid, reduce or prevent their negative impacts on population and environment.
- *Law on Wastes from Industrial Production and Consumption* (1997) aims at fostering efficient management of wastes in order to reduce their amount and increase recycling, reuse and prevent environmental pollution and degradation. It has complemented by the Regulation on the transboundary transport of waste and its disposal (approved by the Government Decision No. 637 of 27.05.2003) which implements the Basel Convention and includes the list of recovery and disposal operations as well as the lists A and B from the Basel Convention and a limited list of categories of dangerous waste.
- *Law on the Environmental Protection* (1993) established a legal foundation for developing normative acts and regulations applicable to different environmental media in order *inter alia* to protect land and subterranean resources, waters and air from "chemical, physical and biological pollution, and from other impacts". It has complemented by the daughter laws and codes on air, water, soil, entrails, natural resources, environmental expertise and EIA and others legislative and normative acts.

The above mentioned legislative acts are complemented by other normative acts, including Sanitary Regulation on storage, neutralization, use and burring of toxic substances and wastes etc.

Pesticides legislation

Pesticides are extensively regulated with legal acts covering main aspects of pesticides management and other standards and acts that indirectly affect pesticides management. These main acts are the Law on Plant Protection (1999), the Law on Products of Phytosanitary Use and Fertilisers (2004) and the Law on Phytosanitary Quarantine (1995). These acts are added by some main regulations such as: the Regulation on the approval and use in agriculture of products of phytosanitary use and fertilisers (1994), the Regulation on management of products of phytosanitary use and fertilisers in the national economy (2003), the Regulation on the testing and approval of products of phytosanitary use and fertilisers for use in agriculture and forestry (2005), the Regulation on the import, storage, marketing and use of products of phytosanitary use and fertilisers (2005) and other acts.

Licensing / authorizing activity legislation

Law on Licensing Certain Types of Activity (2001) is main legal act related to licensing of activities, including activity related to industrial chemicals and pesticides. It seeks to define legal, organizational and economic foundation and scope of the licensing activity. This act is added by the Order of License Chamber on the statement of license conditions and lists of the additional documents, annexing to the applications for licensing for certain types of activity (2006) and other acts on authorization of activities.

Standardization, production safety and consumers rights protection legislation

Requirements on safety of products, equipment, processes, technologies, potentially dangerous systems of manufacture and works, its certification, place in market and protection of consumers right have covered by the following acts: Law on Standardization (1995), Law on Consumers Rights Protection (2003), Law on the Evaluation of Products Conformity (2004), Law on the General Safety of Products (2006) and Law on the Technical Regulation (2006). These acts are complemented by Government's Decision on Nomenclature of production subject obligatory certification of conformity in regulated area (2004) and other normative acts.

Civil protection legislation

The main legal act in this field is Law on Civil Protection (1994). This act is complemented by some by-lows acts, including the Regulation on national network of supervision and laboratory control of environment pollution by radioactive, poisonous, intensively acting toxic substances and biological agents, the Regulation on the order of selection and informational exchange in the protection of public and territory area in conditions of the exceptional situations and others.

Health and labour protection legislation

Protection of labour and human health has covered by following legal acts: Law on Labour Protection (1991), Law on Labour Inspectorate (2001), Labour Code (2003), Law on Health Protection (1995) and Law on Sanitary-Epidemiological Protection of the Population (1993). These legal acts are complemented by some main regulations such as: Hygienic Norms on residues of phytosanitary use preparations in environmental objects, Regulation on conditions and procedure of realization of hygienic certification of the goods, food and non-food products, Regulation on conditions and procedure of reception of the sanitary permit on the right of functioning of objects of national economy etc.

Goods import / export / transport legislation

This legislation has covered by Law on Control of Export, Re-export, Import and Transit of Strategic Goods (2000), Rules on transportation of dangerous goods at territory of the Republic of Moldova and other acts.

International Agreements Status and Coordination

National POPs Strategy, Stockholm Convention NIP and listed above legal acts are complemented by laws on ratification or accession of the Republic of Moldova to the multilateral environmental agreements, regulated chemicals and its wastes, such as:

- *Stockholm Convention on Persistent Organic Pollutants (Stockholm, 2001)* – Law on Ratification of the Stockholm Convention on Persistent Organic Pollutants, No. 40-XV of 19.02.2004.
- *Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal (Basel, 1989)* – Parliament Decree on Accession of the Republic of Moldova to the Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal, No. 1599-XIII of 10.03.1998.
- *Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade (Rotterdam, 1998)* – Law on Accession of the Republic of Moldova to the Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade, No. 389-XV of 25.11.2004.
- *Protocol on Persistent Organic Pollutants to the Convention on Long-range Transboundary Air Pollution (Aarhus, 1998)* – Law on Ratification of the Protocol on Persistent Organic Pollutants and the Protocol on Heavy Metals to the Convention on Long-range Transboundary Air Pollution, No.1018-XV of 25.04.2002 and others.

In 2003, being the Party to the Aarhus Convention on Access to Information, Public Participation in Decision-making and Access to Justice in Environmental Matters, the Republic of Moldova signed its Protocol on Pollutant Release and Transfer Registers.

The Ministry of Ecology and Natural Resources has been designated as competent authority for coordination on implementation of these chemicals MEAs.

NIP Principal Directions of Activity related to POP Pesticides

Based on needs assessment and acknowledging that meeting the Stockholm Convention requirements is an important step towards ensuring the overall national chemical safety the strategic approaches of Moldova in pesticides field has been formulated as follows:

- Increasing capacity for better management of prohibited pesticides.
- Repackaging and centralization of obsolete pesticides.
- Low-cost, community based urgent actions for abandoned deposits.
- Removing old DDT stocks
- Assessment of final solution for obsolete pesticides and abandoned deposits.
- Remediation of Cismichioi pesticide dump and others.

NIP Other Main Directions of Activity related to POPs, including pesticides

Other directions of activities related to POPs, including pesticides, management are:

- Strengthening legal and regulatory framework.

- Increasing POPs monitoring capacity and promotion of research and developments.
- Increasing preparedness for contaminated sites management.
- Public information, awareness and education etc.

Other Relevant Strategic Approach for Obsolete Pesticides Management

It is necessary to mention that the NIP is consistent with the national sustainable development strategy and programs aiming at harmonizing economic, environmental and social aspects of development.

The implementation of NIP listed directions of activities for realization of POPs pesticides problems effectuates in close coordination with other relevant strategic approach related to obsolete pesticides management, such as:

- Strategy on Economic Growth and Poverty Reduction for 2004-2006, approved by Law No. 398-XV of 02.12.2004.
- National Programme on Production and Domestic Wastes Management, approved by Government Decision No. 606 of 28.06.2000.
- Additional Measures for Centralizing Storage and Disposal of Obsolete Unused and Prohibited Pesticides, approved by Government Decision No. 1543 of 29.11.2002.
- National Programme "Moldavian Village", approved by Government Decision No. 242 of 01.03.2005.
- Action Plan Republic of Moldova – European Union, approved by Government Decision No. 22.04.2005 and other relevant acts.

Some results of harmonized activities on implementation of NIP and other acts

Recognizing the importance of the Stockholm Convention and NIP implementation and major effects of harmonized process its implementation in close coordination with other relevant approach and measures for public health and the environment, the Republic of Moldova has effectuated the following activities till this moment:

- strengthened some legal and regulatory acts;
- elaborated strategies, programs and plans on environment and health protection with inclusion of chapters in field;
- established links between ministries and other institutions in this filed;
- increased public information and awareness etc.;

The Republic of Moldova has established national systems and networks for:

- selection and exchange of information in the protection of public and territory in emergency situations;
- observations and laboratory control of environment pollution by poisonous, intensively acting toxic substances and other substances and preparations;
- control of the transboundary transport of dangerous wastes and its disposal;

Other important activities have been undertaken, such as:

- organized POPs environmental and sanitary-hygienic monitoring in water, bottom sediments, precipitations and soil;
- amended statistical form on air pollution with inclusion of relevant items related to POPs registration;
- repackaged and centralized stored the most part of obsolete pesticides;
- transported to France for disposal more than 400 tons of POPs pesticides and other pesticides contaminated by POPs;
- effectuated some measures for insurance of safe storage of dumped pesticides at Cismichioi pesticide dump site and organized permanent monitoring;
- applied for international aid for the strengthening of the national capacity to implement Stockholm Convention and NIP etc.

Principal Environmental Projects for NIP Implementation

Implementation of the NIP activities does foresee mobilization of the financial resources from international donors and as a result all activities are directly linked with available resources both at the international and local level.

Since October 2004 when the POPs Strategy and NIP have been officially approved by the Moldovan government part of activities has been started and being implemented within investments projects supported by international organizations such as GEF, WB, CIDA, NATO, international NGO's and others.

Completed and ongoing projects for NIP implementation are as follows:

- ***GEF-PPG No. TF053700*** "Grant for Preparation of Sustainable Persistent Organic Pollutants (POPs) Stockpiles Management Project"

- *Completed in 2005*
- *Coordination: MENR*

- ***GEF-PPG No. TF055875*** "POPs Stockpiles Management and Destruction Project"

- *Duration: 2006 – 2009*
- *Coordination: MENR*

- ***TF 090384*** "Canadian Grant for the Remediation of POPs Pesticides Polluted Areas and Clean-up of PCB Contaminated Oil in Power Equipment"

- *Duration: 2007 – 2008*
- *Coordination: MENR*

Other Relevant Projects

- ***MILIEUKONTAKT OOST-EUROPA regional project*** "Elimination of acute risks of obsolete pesticides in Moldova, Georgia and Armenia"

- *Duration: 2005 - 2007*
- *Coordination: MAFI*

- ***NATO/PpP-OSCE/ENVSEC Project*** "The destruction of pesticides and dangerous chemicals in the Republic of Moldova"

- *Coordination: MD*

Further projects

- *Moldova / UNEP Partnership* on Capacity Building for Improving the Environmentally Sound Management of Chemicals (SMC) in the Republic of Moldova and the Implementation of SAICM

- *Duration: 2008 – 2009*
- *Coordination: MENR*

NIP Implementation Problems

At the same time the country has confronted with a number of problems during the implementation of the Stockholm Convention and NIP such as:

- lack of uniform established system and sufficient capacity for sound management of chemicals;
- some gaps admitted during NIP elaboration and short NIP duration;
- insufficiency of legal, institutional, technical and human capacity;
- insufficiency of inter-ministerial coordination, some barriers and competition between institutions;
- fragmented responsibilities across institutions as well as duplication of activities and others.

Needs for liquidation of problems

Taking into account the above mentioned the Republic of Moldova should take lessons and undertake the following measures for improvement of the activity and achievement of the purposes stated in the international agreements and the strategic documents on their implementation, namely:

- strengthen capacity on sound chemicals management throughout their life-cycle;
- effectuate NIP review and updating;
- mobilize resources for implementation of NIP and other relevant international agreements;
- strengthen of national legal, institutional, technical and human capacity;
- establish and maintain partnerships, bilateral and/or regional co-operation;
- strengthen national stakeholder participation from outside of ministries/institutions and develop harmonized national position related to obligations covered by MEAs etc.

Implementation Benefits

Learned lessons, realization of measures for liquidation of gaps, coordinated activity and cooperation inevitably will result benefits, achievement of goals and solution of tasks following from the NIP and other relevant documents, such as:

- developed sound management of chemicals throughout their life-cycle, strengthened legal, institutional, technical and human capacity, NIP reviewed and updated;
- resources attraction and mobilization;
- liquidated gaps in the national policy and activity related to POPs, other chemicals & wastes management;
- strengthened coordination / relationship / understanding of different issues, and liquidated isolation / barriers / duplication and identified and reinforced common position on mentioned issues;
- improved and increased efficiency, cost-effectiveness, and transparency;
- reduction of pollution / risks / damage and others.

POPs STOCKPILES MANAGEMENT AND DESTRUCTION IN MOLDOVA

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Since 2006 the Ministry of Ecology and Natural Resources has been implementing in Moldova the Persistent Organic Pollutants Stockpiles Management and Destruction Project financed by the Global Environmental Facility through the World Bank. This Project is succeeding the Enabling Activities for the Implementation of the Stockholm Convention in the Republic of Moldova Project, carried out in 2002-2004 and aimed at developing the National Plan for the Implementation of the Stockholm Convention.

The general objective of the project is to protect the environment and human health by safely managing and disposing of stockpiles of obsolete pesticides from agriculture, containing or contaminated with Persistent Organic Pollutants (POPs) and the equipment from energy sector contaminated with Polychlorinated Biphenyls (PCBs). The project envisages shipment and destruction abroad of about 1150 tons of obsolete pesticides out of the 3000 tons in the warehouses and about 1060 tons of power capacitors containing PCBs. The project goal is to strengthen also the regulatory and institutional framework for long term control of POPs and other toxic substances in line with the requirements of the Stockholm Convention and other related conventions and protocols ratified by Moldova.

The project is implemented under the Ministry of Ecology and Natural Resources, in cooperation with the Ministry of Agriculture and Food Industry, Ministry of Industry and Infrastructure, Ministry of Defence and other stakeholders from private sector. The project activities are carried out by consulting companies and consultants from abroad and from the Republic of Moldova.

The outcomes of this project will be reduction of POP pollution risks on the environment and human health, setting up at the national level of one modern regulatory system for management and control of POPs and other toxic and dangerous chemicals and wastes, and strengthening the national institutional and human capacities for sustainable development of POP stockpiles.

The project activities are complemented by the activities of Canada POP Fund financed project, NATO financed project, implemented by the Ministry of Defence; "Energy II" GEF financed project, implemented by the Ministry of Industry and Infrastructure; „Milieukontakt-International" project financed by Dutch government and implemented in Hincesti district etc.

Dangerous chemicals and their handling

The negative effects on the environment and population health, caused by improper management of chemicals in various sectors of the economy, have raised in the last years more serious concerns at global level.

Our country is not exception. Moldova is not producing dangerous chemicals but has used in the past and is still using such materials in different sectors of the economy and although Moldova is a small country, the population density is the highest in the region. This increases the risks generated by various natural or anthropogenic negative phenomena and especially by harmful effect of dangerous chemicals. That is why environmental problems are more seriously approached by the government.

There is a good perception in the country that the sound management of dangerous chemicals is one of the most important environmental and social problems.

The Republic of Moldova position on environmental problems is reflected in country commitments after adhering to and ratifying 18 international environmental conventions and other bilateral and multilateral agreements on the environment and human health protection. Among them there are also ones which regulate the activities with dangerous chemicals and particularly with persistent organic pollutants (POPs).

The Republic of Moldova ratified the Stockholm Convention on persistent organic pollutants on 19th February 2004. The National Strategy on reduction and elimination of persistent organic pollutants and the National Plan for Implementation of the Stockholm Convention have been approved in the same year.

In 2002 Moldova ratified also the Aarhus Protocol on Persistent Organic Pollutants of the Convention on the Long-range Transboundary Air Pollution, Geneva (1979). Moldova adhered to the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal (1989), the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade (2004).

The dangerous chemicals related issues are reflected in several national long-term policy and programme acts on poverty reduction and environment protection, including:

- National Program for Industrial and Consumption Wastes Utilization (2000)
- National Environmental Health Action Plan (2002)
- Concept of the Environmental Policy of the Republic of Moldova (2001)
- A number of governmental decisions, including Governmental Decision no. 1543 from 29th December 2002 on additional measures for centralised storage and neutralization of obsolete pesticides
- The Economic Growth and Poverty Reduction Strategy Paper (2004)
- National Development Strategy for 2008-2011 (2007)

This shows Moldova serious commitment to solve environmental problems at national and international level.

Our country is currently missing the capacities to solve solely the existent environmental problems. In this respect, the technical assistance offered to Moldova by international organizations through various environmental programmes is an extremely important contribution to the process of reduction of dangerous chemicals in the country and in the region.

Complex actions in this respect are taken by the Ministry of Ecology and Natural Resources through the projects managed by POP Sustainable Management Office, as well as other institutions and organisations under similar projects. The general objective of such activities is environment protection and human health by environmentally safe management and disposal of stockpiles of chemicals, containing or contaminated with persistent organic pollutants, remediation of contaminated sites, improving the legislative and institutional framework for a long term control of them and other toxic chemicals according to requirements of the Stockholm Convention and other relevant conventions and international agreements ratified by Moldova.

Reduction of the obsolete pesticides pollution related risks

According to Government Decision, the Ministry of Defence and the Ministry of Agriculture and Food Industry are responsible for primary repacking and centralised storage of obsolete pesticide. In 2003-2005, according to Government decision no.1543 from 29.11.2002, the special units of the Ministry of Defence and Department for Emergency Situations have repacked and stored about 2000 tons of obsolete pesticides in 22 districts. Funds for such activities have been allocated from the state budget and National Ecological Fund, counting circa 5 million lei. Further on the Project on destruction of pesticides and dangerous chemicals, financed by NATO/OSCE and implemented by the Ministry of Defence continued these activities in 2006-2007. As a result, 3250 tons of pesticides have been stored in centralised warehouses. Also, in summer-autumn of 2007, another 36 illegal burial places with obsolete pesticides were identified. The total quantity of such chemicals in 12 administrative-territorial units is estimated at more than 260 tons. The Ministry of Defence have been appointed as responsible for digging out, repackaging and storing of new found pesticides. The National Ecological Fund allocated 800 thousand lei for such activities.

Management and disposal of stockpiles of persistent organic pollutants

The GEF/WB Persistent Organic Pollutants Stockpiles Management and Destruction Project has engaged to reach considerable results in solving environmental problems in Moldova This project was launched in February 2006, as a GEF/WB grant of 6.35 million dollars, including 3.72 million dollars as a counterpart contribution from the state budget and National Ecological Fund.

The project has been developed under the Ministry of Ecology and Natural Resources. The project development process succeeded due to a close cooperation with the stakeholders and the support from the Government of Moldova and the World Bank.

The donor decision to grant the project owes to Moldova commitment to take concrete measures to conduct for the global community the duty resuming from signing the Stockholm convention and other international agreements in the field.

In this regard an importance gained in 2003 the state funding of the activities to minimize the impact of polluting the environment through carrying out the repackaging and centralized storage of obsolete pesticides, accumulated in the previous years in former agricultural collective farms. Another prove of serious approach of environmental issues was the availability of Moldova Government to co-finance the WB/GEF project with the funds form the state budget and the National Ecological Fund, including the elimination and disposal of pesticide wastes.

It was also appreciated the successful implementation of previous projects, financed by the GEF, through the World Bank, which resulted in developing, approval and signing by Moldova, as a first country, of the National Implementation Plan for the Stockholm Convention.

The project is implemented under the Ministry of Ecology and Natural Resources in cooperation with the Ministry of Agriculture and Food Industry, Ministry of Industry and Infrastructure, Ministry of Defence, other interested parties from the public and private sector. The GEF/WB activities are complemented by other two ongoing or recently started projects in the field.

As a result of GEF/WB project implementation about 2000 tons of wastes containing or contaminated with POPs will be eliminated and disposed of. The optimal solution was taken so as the pesticides will be incinerated in special facilities of one of the western countries having capacities; modern and environmentally safe technologies licensed to undertake such work. This solution was proposed and accepted as a result of a detailed analysis of some alternatives undertaken during project development, considering economic, ecological, technological, social aspects.

TREDI S.A., a French company, was contracted to carry out the work. NIRAS Company from Denmark is supervising the compliance of the works with European standards and requirements of international agreements.

Repackaging, elimination and destruction of 1150 tons of obsolete pesticides from 12 warehouses, in 10 districts, was launched in March 2007. Further on, TREDI shipped to its facilities from France more than 800 tons of waste from Telenesti, Hincesti, Straseni, Nisporeni, Floresti, Soldanesti, Riscani and Briceni and disposed of. It is estimated that the elimination of pesticides from Stefan-Voda and Cimislia will be finished by the end of April 2008

In energy sector the dismantling/excavation, elimination and destruction of the power capacitors containing polychlorinated biphenyl from the power stations of State Enterprise “Moldelectrica” took place in October 2006-September 2007. TREDI S.A. has shipped to France and disposed of more than 18 000 capacitors (934 tons).

Besides the supervision of elimination and disposal of POP wastes, NIRAS Company has carried out a “Vulcanesti 400kw” power station clean up feasibility study report to identify the level of PCB pollution after removing the capacitors. Based on this study some recommendations for cleaning-up the area will be made and the quantity of soil contaminated with PCBs at a level higher than 50 ppm identified. About 2500 tons of polluted soil has been depicted to be shipped to France and disposed of, exceeding the initially envisaged quantity of 50 tons. In the light of these events, at NIRAS suggestion, “Moldelectrica” administration and the Project Management Team find the elimination and disposal abroad of just part of contaminated soil improper. They found the collection and storage of contaminated soil on the station territory as the most technically, economically and ecologically viable. The soil will be collected and contained in specially designed cofferdam provided with liners and protective soil layer to avoid pollution penetration in the environment and to ensure thus permanent monitoring of these stockpiles.

Improving the national legislation on POP

The current legislation will be improved and the POPs management capacities will be strengthened mainly based on the Stockholm Convention requirements and oriented to a wider approaching of chemical safety in the country, to developing at the national level of modern regulatory system for management and control of such and other chemicals as well as toxic and hazardous chemical wastes and consolidating the institutional and human capacities for sustainable management of POPs stockpiles. During project implementation it is envisaged to transpose the relevant EU legal acts in the national legislation.

The amendment of legal and regulatory framework on POPs started in August 2006 and is carried by COWI, a Dutch company. Considering that the task depends mostly on the contribution and participation of MENR and other ministries, departments, institutions specialists working with POPs issues, the objectives and activities planned have been presented in details at a workshop to launch the activities and the contacts among all the stakeholders established.

COWI has later performed the analysis of the national legislation in the field to highlight the legal gaps and upgrade the legal and regulatory framework. The results of this task have always been discussed and coordinated with the specialists from the institutions involved and reported to the National Coordinating

Committee. There have been developed and approved the Report on gap analysis of the national legislation (Legal Gap Analyses Report) versus European legislation in the field and international agreements Moldova is part to and the Legal Development Plan on POPs.

COWI use this Plan as a background for developing the legal and regulatory acts, regulatory mechanisms and relevant instructions. At initial stage priority is given to developing the PCB Regulation and supporting instructions and to preparing general information about Requirements for information management and Requirements for POPs management reporting stipulated in EU legislation. These documents are necessary firstly because they are linked to other two project tasks on inventory of PCB containing or contaminated equipment and on development of Management Information and Reporting System should be launched in 2008. The task for POPs national legislation improvement will be completed in October 2008.

Strengthening the capacities for POPs management

Strengthening the capacities for POPs management imply some measures for strengthening the subunits of the Ministry of Ecology and Natural Resources as the central authority for coordination and implementation of Moldova's international obligations of under the Stockholm, Basel, Rotterdam conventions and other international agreements on POPs, strengthening the inspectorates in order to apply the regulations on POPs and upgrading and improving the capacities of the laboratories to identify the POP content in the environment.

The laboratory of Hydrometeorological State Service will be upgraded with the equipment purchased under the POP stockpiles management and destruction project and equipped to perform the PCB analyses at international level.

Additionally to this, in 2005-2007 under the NATO project, implemented by the Ministry of Defence some equipment was purchased and the laboratory of the State Centre for testing and certification of fitosanitary products and fertilizers, of the Ministry of Agriculture and Food Industry was re-equipped. The laboratory has presently modern capacities to analyse the pesticides.

Along with improvement of legal and regulatory framework for elimination and minimization of the POPs-generated risks to the environment and human health there have been promoting the best practices for pesticides management in crop production, actions to improve the pesticides procurement and import procedures. The trainings for farmers and farmer associations and public information campaigns have been organised and the relevant guidelines and other informative materials published under the IDA RISP II project since 2006.

In order to coordinate the activities and promote the implementation in Moldova of POPs and hazardous chemicals management policies, the POPs Sustainable Management Office have been created in the Ministry of Ecology and Natural Resources (Order no. 22 from 20.03.2006). The Office supports MENR in coordinating the POPs and hazardous chemicals management activities with other governmental agencies responsible for regulating, managing and controlling the POPs and hazardous chemicals, in managing and coordinating the National Implementation Plan for the Stockholm Convention implementation. The Office intiate and undertake projects in this field and coordinates its activities with those from other similar ongoing projects in Moldova.

Currently, both with POPs Stockpiles Management and Destruction Project, the Office is implementing the other two projects:

– Canadian Grant for the Remediation of POP Pesticides Polluted Areas and Clean-Up of PCB Contaminated Oil in Power Equipment, financed by POPs Canadian Fund through the World Bank *and*

– "The Moldova and UNEP Partnership on Capacity Building for Improving the Environmentally Sound Management of Chemicals (SMC) in the Republic of Moldova and the Implementation of SAICM", financed by UNEP.

The remained activities for strengthening the capacities for POPs management, including development and upgrading of the Information Management System, POPs Reporting System and POPs Monitoring Network; identification of POP residues and mapping of polluted areas; inventory at the national level of power equipment contaminated with PCBs will be launched this year.

POPs Awareness and Educational Activities

One of the important tasks of the project is creation of a general communication framework on POPs and other chemicals in order to increase the level of awareness of the public at large and the specialists about POP sources and their effects through undertaking information campaigns and training and involvement of target groups with high risks with higher exposure to POPs risks. The activities to carry out the above mentioned tasks started in June 2007 and comprise: evaluation and monitoring of public awareness level on POPs issues; training and education; radio and TV broadcasts; development and publication of posters, promotional materials, guidelines for NGOs and target groups; design, development and maintenance of the project web-site. To carry of these activities five local consulting companies have been contracted, including INQUA-Moldova, Regional Environment Centre, Environmental Movement from Moldova, Garomond Studio Inc. and Casa Imago Inc.

SUPERVISION OF POPS REPACKAGING AND DISPOSAL ACTIVITIES – EXPERIENCES FROM AMONG OTHERS THE MOLDOVA POPS PROJECT

Preben Røgild KNUDSEN[1], Corneliu BUSUIOC[2]

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The paper will be presented by senior consultant Mr. Preben R. Knudsen from NIRAS Denmark - Project Manager for NIRAS on the present Moldova PCB and Obsolete Pesticide repackaging and export for disposal Project and Mr Corneliu Busuioc, Moldova local supervisor and expert, sub-consultant to NIRAS on the Moldova project.

Mr Preben R. Knudsen will present his experiences and lessons learnt as Project Manager from other supervision of international POPs repackaging and disposal projects and present the overall set-up of the management, supervision and monitoring system for the Moldova project. The paper will reflect the experience gained in reaching the project's specific objectives, particularly: Ensuring environmental sound packaging, transportation and destruction of 1,150 tones of obsolete pesticides and 17,300 obsolete PCB-containing capacitors; ensuring the contractor protect the health and safety of workers and the public in undertaking the removal, packaging, transportation and destruction POPs; assessment of the extent, impact and risks of PCB contamination remaining at the Vulcanesti substation, where the major part of the contaminated capacitors were located; recommendations on the future cleanup of the Vulcanesti substation site.

Mr Corneliu Busuioc will present some of his experiences from the supervision of the repackaging of PCB contaminated capacitors and Obsolete Pesticides in Moldova. Including some lessons learnt from the actual work as local supervisor acting in between the project owner and recipients (Moldovan government representatives), the International contractor (TREDI) and the international supervision consultant (NIRAS).

Keywords: Project Documents, Lessons Learned, Local Consultant, Communication, Documentation.

NIRAS – by Mr. Preben R Knudsen

NIRAS is a Danish multidisciplinary consulting engineering and planning company with high ranking experiences in Environmental protection issues and has around 1000 employees and more than 150 of these have experience from working outside Denmark.

NIRAS has long time experience working with projects regarding POPs and cleaning up contaminated sites. Senior Consultant Preben Røgild Knudsen has long time experience from working with environmental as well as solid wastes projects and since 2000 he has been working with POP projects in Mozambique, Senegal, Mauritania and Cape Verde and now as project Manager and Overall Supervisor on this project in Moldova.

MOLDOVA POP MANAGEMENT AND DESTRUCTION PROJECT

Overall Project Objective

This project is part of an overall project for Management of POPs in Moldova consisting of three elements:

1. Management and destruction of POPs
2. Strengthening the Regulatory Framework and Capacity Building
3. Institutional Strengthening and Project Management support

Project Objective

The part NIRAS involved is addressing the overall project objective 1 regarding packaging, transport and final destruction (incineration) of the POPs and consists of two elements:

1.1 Management and Destruction of 1,150 tonnes of Obsolete Pesticides stockpiled in 12 warehouse around Moldova

1.2 Management and destruction of around 19,300 PCB contaminated capacitors (around 1,000 tonnes) at 13 sub-stations and 50 tonnes soil at Vulcanesti as well as preparation of a plan for future clean up and re-mediation at the contaminated sub-station Vulcanesti

Project Consultant - Objective

NIRAS is hired as consultant with the objective to provide advisory to the Moldovan Project Management Team (PMT) and the involved ministries responsible for the POPs regarding execution of the project including supervision of the Turnkey Contractor (TREDI S.A., France) hired by PMT to be responsible for packaging, transport and final disposal of the POPs.

NIRAS has formed a team consisting of 4 experts from NIRAS including Project Management, two external international experts and a local expert Mr Corneliu Busuioc from Moldova responsible for the day to day supervision of work.

CONTENT OF THIS PAPER

- Mr Preben R Knudsen will present the overall set-up status for implementation of the management, supervision and monitoring system for the Moldova project and his experiences and lessons learnt seen in the context from management and supervision of other international POP projects.
- Mr Corneliu Busuioc will present some experiences from supervision of the project.

MANAGEMENT AND STATUS THE MOLDOVA PROJECT

Following documents have been prepared and used during the execution of the project:

1. Inception Report by NIRAS. Describing any needed changes in project implementation after contracting the works turnkey contractor and the consultant.
2. General Work Programme (GWP) and Site Specific Work Programmes (SWP) by TREDI. Describing how the work will be performed by the Turnkey Contractor including: a) Managerial aspects; b) Emergency procedures; c) Staff Welfare (incl. PPE); d) Site Rules and e) Transfer of Dangerous Goods.
3. Review of GWP and SWP by NIRAS. Including recommendations for changes.
4. Supervision Manual by NIRAS corresponding to the GWP and SWP.
5. Inspection of Disposal Facilities in France by NIRAS.
6. Monthly Progress Reports by NIRAS during field work including: a) Progress of works (amounts in tonnes and MDL); b) Variation in works (time table, problems, claims).
7. Project Completion Reports by TREDI including disposal certificates.
8. Supervision Completion Reports by NIRAS (Progress Report).
9. Pre-excavation Report for Vulcanesti by NIRAS, describing how the buried capacitors at Vulcanesti substation should be excavated.
10. Post-excavation Report for Vulcanesti by NIRAS, with final site risk assessments for future clean up activities.
11. Vulcanesti Substation Cleanup feasibility Study Report by NIRAS with recommendations for future clean up activities.

All activities are in progress and are expected to be finalised in autumn 2007. All PCB wastes have been repacked and removed from the 13 substations, buried capacitors has been excavated at Vulcanesti and re-packaging of obsolete pesticides is expected to be finalised in September 2007.

LESSONS LEARNED

In the West Africa POP project in Senegal, Mauritania and Cape Verde a lessons learned report was produced by NIRAS together with the other involved parties the Recipient countries and the donors, The Royal Netherlands Embassy in Dakar and Croplife as well as the Turnkey Contractor.

With the aim of giving a total picture of how I presently see lessons learned from POP clean up projects this paper combines the lessons learned from the West Africa Project, the Mozambique project and this project in Moldova despite of course you have country differences between especially Africa and Europe.

The lessons learned are structured after the steps in the project cycle from first step in choosing a consultant until final step disposal of the POPs. For each project cycle step (1-9) lessons learned (recommendations) from each issues for review is listed

Issues for review	Lessons learned (recommendation)
1. Project consultant	
Consultant availability and expertise	*The expertise includes: Production of project proposals, Undertaking of inventories, Training, Tendering and contracting, Project monitoring, Problem solving.* The undertaking of tendering is best done by a specialist tendering expert/resource

Issues for review	Lessons learned (recommendation)
	but it needs to have good experience of these projects and their needs and it is recommendable that tendering and supervision of works contracts are done by same consultant.
2. Local Government counterparts and communications	
Involvement and calibre of local counterparts	Local Liaison Officers (LLO) of high calibre and ability must be assigned by the recipient countries and participated from the stage of the project kick-off.
E-mail communica-tion failures during project implementa-tion	It is very important that a reliable e-mail communication system is established before project start and that all parties are aware of keeping the system operational during project implementation. If government links prove unreliable then contingency links should be arranged
3. Coordination and planning	
An efficient time planning tool should be used	These projects are complex undertakings involving multiple and inter-related steps. The use of a common (software available for all project parties) enables all parties to monitor progress and to foresee the consequences of, and to plan for, any deviations that might occur.
Transportation problems can delay the field work.	A more detailed logistical study for personnel and equipment is required for countries with bad infrastructure. A contingency should be built into timing.
4. Inventory	
How to ensure that the country inventory is complete and how to plan for variations?	1. The inventory scope should include quasi- and non-governmental major pesticide users within a country. 2. Following are included during the preparation of the inventory: • Identify location of store by using gps. • Sketch hand drawing of each store. • Digital pictures from outside and inside each store corresponding to the sketch drawing. • Digital pictures of each waste lot (pesticides, related waste and contaminated soil), showing the location. • The sketch drawings and a table with picture numbers referring to the drawing and each waste lot should be included in the Site Report for each site. • A walk-round video (on cd-rom or DVD) of sites with commentary would prove valuable. • Is prepared as a database or spreadsheet that can be interrogated (sorting by product name, supplier, location etc) and that it is available for all project parties. • That the summary tables for each store in the inventory can be directly transferred to the Progress Reports, Site Reports, Taking Over Documents (TOD) and the Handing Over Documents (HOD) (e.g. word documents) 3. A good contingency needs to be built into the project budget to cater for additional stocks being found during the implementation phase.
Securing stocks after inventory-taking	1. If during the inventory a potential risk of theft of stocks is identified then steps should be taken to make the stocks more secure. 2. There should be the minimum of time between undertaking the inventory and carrying out the fieldwork
5. Tendering and contract	
Pre-Qualification announcement shall include	• That it will not be accepted that pre-qualified tenderers subsequently form joint ventures with other pre-qualified tenderers, • That if a Contractor wishes to use a sub-contractor for the field work, the

Issues for review	Lessons learned (recommendation)
	name, qualifications and experience should be described in the pre-qualification application.
Are pre-tendering site visits by the potential contractors necessary?	Instead of pre tendering site visits it would be simpler and more cost effective for a detailed video to be produced during the inventory stage and for this, and the usual library of digital photographs, to be provided to bidding companies to assist bid preparation.
The sub-contracting of field work and the associated administrational performance	1. Risk is minimised when the hazardous waste companies undertaking this kind of project have their own field teams. 2. During the tender assessment process there should be special attention paid to a company's past administrational performance (report writing, communications, adherence to procedures etc)
6. Notification and Mobilisation	
Delays with custom clearance of equipment and packaging material	1. The national custom regulations of the project country should be checked and the relevant procedures should be well prepared. 2. The Local Government Representative has to become actively involved in the facilitation process right from the start. 3. The field team deployment should wait for the confirmed customs clearance.
Failure to implement fully agreed procedures	1. The use of sub-contractors for essential parts of work (especially the field work) must be carefully assessed as part of the tender and contract evaluation. If a sub-contractor is accepted, means of enforcement of the contract conditions (procedures) for both the Contractor and the Employer should be included in the contract.
7. Field Work	
Data security and back-up	The contractor should download and backup documentation (records photos etc) daily
Special provisions if night work is required	During fieldwork planning it should be decided whether working at night might be required and in these cases the necessary lamps, cables, generator etc should be included in the equipment.
8. Shipment and transport in Europe	
Procedural failings prior to exportation of the stocks.	The stowing of containers should be approved by the shipping company and documentation for this approval forwarded to the Project Manager **before** the field-work contractor leaves the country.
Some labelling of sea freight containers was not adequate	1. A final check on labelling should be made by the Contractor before departure and after arrival at port of importation 2. Labels of adequate quality and adherence must be used.
9. Incineration	
Some waste had to be repacked before incineration due to the high sulphur content.	When contractors can feed drums directly into their incinerators it is desirable that the waste should be packed directly into such drums in the field. The small units will increase costs of repackaging but this can be offset to a degree by reduced transport costs (if closer packing proves possible) and by the reduced handling risk.

LOCAL CONSULTANT– by Mr. Corneliu Busuioc

The overall task of the local supervisor is the day to day supervision of the execution of the Works Contractor. Particularly, collect and check works contractor documentation and reports, supervise the execution of the General and Specific Contractor's Work Plans, support PMT, Project Owner (Government institutions responsible with disposal of the POPs) in monitoring the implementation of the works.

Observations made from local perspective regarding some of the projects activities are suggested as topics to be considered while planning POPs disposal projects in the future. Observations and recommendations are presented in the table below and are grouped as: Communication/Coordination, Local commitment, Using past experience.

Observations / Issues for review	**Lessons learned (recommendation)**
	Communication / Coordination
Knowledge of local administrative requirements / procedure	*In the beginning of the project the contractor's plans did not consider time needed for a local decision making (e.g. approval of General Work Plan for packing and transportation works by Central Authorities - Department of Emergency Situations and Ministry of Health (occupational security)). This was one of the reasons to postpone the already agreed date of works launch.* The local counterpart should provide advice to the works contractor in terms of local decision making process in order to include the time needed for this in contractor's time schedule. Also, it is meaningful to have in the team a local expert/advisor to the manager with relevant knowledge/experience in local administrative procedures pertinent to the project.
Coordination between different donors within Moldova POPs project on-besides other aspects - the technical aspects of works execution.	*Packing of the Obsolete Pesticides in Hincesti warehouse have been financed and Project executed by Dutch NGO "Millieucontact"* It would be ideal that parties have been coordinated the way of packing the OP. As for instance the way the OP have been packed within the Millieucontact Project in Hincesti makes the transportation less efficient and quite expensive for the works contractor TREDI (9 tones / truck instead of desired 18 tones) due to the fact that the bags are too small.
Regular coordination meetings.	With participation of all main involved parties would very much enhance planning process and the works execution efficiency.
	Local commitments
Local institutions awareness about their in kind contribution to the project	The main counterpart should pay more attention in making its subordinated institutions aware about their role and function in providing local contribution as agreed and stipulated in the project document.
Problems with security of the sites (some PCBs sites missed tens of inventoried capacitors)	The beneficiary institutions have to secure both OP warehouses (plastic drums, metal drums) as well as PCBs capacitors sites (there is a demand for capacitors among the small enterprises) from the risk of theft. All parties should try to minimize time between the inventory completion and start works as well as simply secure guards. Probably this should be part of commitment (in written). If the local interested party fails to cope with this requirement then the responsibility should be financial - the difference between the inventory and actual number (number of capacitors, drums, other goods) should be covered by the local beneficiary (at the unit price specified in Works contract).
	Using the experience from previous projects
Important amount of time (extra time) spent to get the General Work Plans / Specific Work Plans approved	The amount of time spent by all parties to reach the required by the Client level of clarity and specificity of the Work Plans was much more than planned. In this respect a question naturally suggests itself - why not use experience gained during previous similar projects (Work Plans from previous similar projects as templates - assuming that developing of this kind of documents is a mandatory requirement)?

MOLDOVAN PESTICIDE REPACKING & REMOVAL PROJECT – NEXT STEPS

Eric OLTMAN

NATO Maintenance & Supply Agency (NAMSA)

Moldova identified a need to re-pack and centralize stockpiles of obsolete pesticides which were dispersed throughout the country to minimize the potential threat to human health and the environment and reduce the burden placed on the Moldovan Ministry of Defense. NATO developed a project to assist Moldova with these efforts that would focus on the four major components: (1) repacking and centralization; (2) chemical analysis; (3) destruction; and (4) site remediation.

NAMSA was tasked to manage the project on behalf of the joint Lead Nations Belgium and Romania and the other donor nations: Bulgaria, Czech Republic, Finland, Ireland, Lithuania, Luxembourg, the Netherlands, Norway, Sweden, Turkey and Germany. The tasks carried out by the Chemical Defense Unit (CDU) of the Moldovan Ministry of Defense focused on repackaging and transportation of the pesticides. The solid pesticides were packed into 50 kg polypropylene bags and then into plastic drums and the liquid pesticides were decanted into steel barrels.

Repacking and relocation started in November 2006 and progressed well. Samples were analyzed at a NATO Science for Peace Program funded Chemical Analysis Laboratory. There were several incidents including a fire and vandalism at several of the relocation warehouses. The Moldovan MOD was also able to resolve several delays by providing needed packing drums and suitable secure storage. By early July 2007 the Moldovan CDU had completed the repacking and relocation of 1.263 tons from 228 unregistered sites into 21 regional relocation facilities.

The next steps for the project include destruction of the pesticides and site remediation. Options for destruction of the repacked pesticides include export to a special incineration plant, bringing an incineration plant (either temporary/mobile or permanent) to Moldova, or burning the pesticides in a cement plant kiln.

Key Words: NATO, NAMSA, Moldova, Pesticide, Stockpiles, Repacking, Relocation

In April 2003 a requirement to destroy approximately 1,700 tons of obsolete pesticides and other chemicals was identified and NATO assistance was requested. These stockpiles of pesticides included banned chemicals such as Persistent Organic Pesticides (POPs), unidentified material and chemicals made unserviceable as a result of age, contamination or chemical breakdown.

The urgent requirement was to repack and centralize the stockpiles of these chemicals which were dispersed throughout the country to minimize the potential threat to human health and the environment and to reduce the burden placed on the Moldovan Ministry of Defense which guards these sites.

Example Unregulated Storage Facility

Moldovan Ministry of Defense (MOD) involvement was necessary as their Chemical Defense Unit (CDU) provided the only repository of expertise capable of handling the material on as large a scale as faced in Moldova. In addition, responsibility for guarding the sites has also devolved to the military due to recent attempts to steal, use or sell the chemicals.

Four distinct phases within the overall requirement were identified:

Phase 1 **-** Repacking and centralization of the stockpile;

Phase 2 **-** Chemical analysis of the stockpile;

Phase 3 **-** Destruction of the stockpile; and

Phase 4 **-** Remediation of storage sites.

The goals of the NATO project were to complete Phase 1 **-** Repack and centralize identified Moldovan stockpiles of obsolete pesticides and chemicals and Phase 2 **-** Chemical Analysis of the Stockpiles as interim steps towards their final destruction.

NAMSA was tasked to manage the project on behalf of the joint Lead Nations Belgium and Romania and the other donor nations (see Table 1). The tasks carried out by the Chemical Defense Unit (CDU) of the Moldovan Ministry of Defense focused on repackaging and transportation of the pesticides. NAMSA hired a Project Verification Auditor to assist with coordination, communication and verification

Table 1 - Donor Nations
Belgium *
Romania*
Bulgaria
Czech Republic
Finland
Ireland
Lithuania
Luxembourg
The Netherlands
Norway
Sweden
Turkey
Germany
* **-** Joint Lead Nation

Solid pesticides were to be packed into polypropylene bags each containing 50 kilograms of chemical. The bags were to be further packed into heavy duty 120 liter plastic barrels sealed by a rubber lid held in place by a spring collar. Liquid Pesticides were to be decanted into steel barrels with 2.5 cm thick walls of various sizes, 50, 100 or 200 liters depending on the quantity recovered at each site.

The NATO project is part of a larger initiative for the eradication of Persistent Organic Pollutants (POPs) in Moldova. This initiative includes a World Bank project for the disposal of PCBs in electrical transformers and the shipping of 1,150 tons of pesticides and dangerous chemicals to France for incineration by end of 2007.

A formal opening ceremony for the NATO Pesticide Removal project was held in November 2006. The opening ceremonies were well organized and implemented, attracting national and international interest and provided a high profile forum to demonstrate the need for further funding to complete the project. The meeting was well attended, well covered by the media, and included an opening address by the President of Moldova Vladimir Voronin. The event also included the opening of a Science for Peace (SFP) Program funded Chemical Analysis Laboratory and the opening of the Strasenie relocation warehouse.

The Science for Peace (SFP) Chemical Analysis Laboratory was built so Phase 2 of the project – Chemical Analysis of the Stockpiles could be completed. The role of the SPF Chemical Analysis Laboratory was to analyze and identify the pesticides and dangerous chemicals that were being repacked and relocated in Moldova. The laboratory will be funded for two years and SPF will provide further equipment and training. The laboratory was fully functional during the project and provided detailed analysis reports for the project.

The actual repacking and relocation started in early November 2006 in Straseni as 7 teams of the Army's Chemical Defense Unit were deployed across the region. Table 2 below details the progress of the repacking and storage efforts over time. The project generally progressed well. However, it experienced delays due to internal problems related to the provision of repacking materials and the failure to provide suitable relocation facilities by local authorities. The Moldovan MOD was able to resolve these delays by providing the needed packing drums and suitable secure storage facilities which helped the project to be successfully completed.

By early July 2007 the Moldovan Chemical Defense Unit had completed the repacking and relocation of 1.263 tons from 228 unregistered sites into 21 regional relocation facilities. The project was completed in an effective and professional manner without any reported toxic hazard incidents.

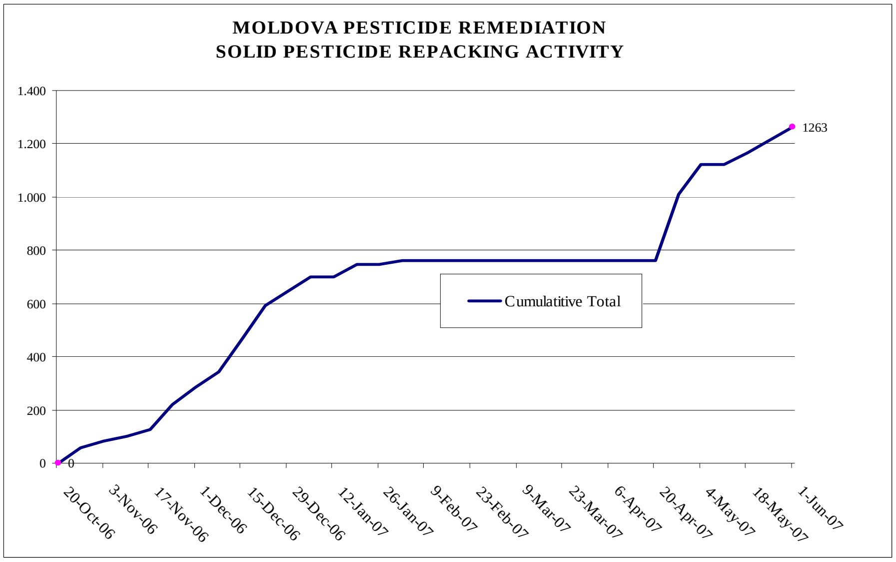

Table 2

Example Storage Facility with Pesticides Repackaged and Stacked

There is a need to complete the remaining two steps of the project as there were several incidents including a fire and vandalism at a couple of the relocation warehouses.

The fire at the Criuleni pesticide storage facility was reported on 17 January 2007. The storage facility held more than 100,000 tons of solid and liquid pesticides previously centralized there by the Moldovan government and nearly 80,000 tons of solid pesticides recently stored there by the Chemical Defense Unit (CDU) of the Moldovan MOD.

In addition, on 14 May 2007 it was discovered that the Cimicioi Relocation Facility had been vandalized and some of the packaging removed as the door and window frames had been previously stolen.

The next steps for the project include Phase 3 – Destruction of the Pesticide Stockpiles and Phase 4 – Remediation of Storage Sites. This is appropriate as the aim of this conference is to determine effective methods for destruction of pesticides and site remediation.

Pesticide Storage Facility Fire - Criuleni

Initial consultations indicated that high temperature incineration was the most likely method for destructtion of the pesticides. Options for destruction of the repacked pesticides include export to a special incineration plant like the one the World Bank used on behalf of the Global Environment Facility in France or bringing an incineration plant (either temporary/mobile or permanent) to Moldova. Another well accepted destruction technology includes the burning of the pesticides in a cement plant kiln.

Exporting the material to countries with the appropriate destruction technology is being used on other projects in Moldova and could be a cost effective solution. Building a permanent incinerator to deal not only with the existing stockpiles but future stockpiles of pesticides and other hazardous waste in Moldova would require a significant amount of investment.

Example Project Activities

Leasing of a mobile incinerator from specialized companies and transporting it to Moldova to carry out the destruction could be achievable. However any incineration would generate a significant amount (30% of gross weight) of waste material that had to be disposed.

Using a cement plant kiln to destroy the pesticides is a preferred option globally for the destruction of pesticides for both technical and cost reasons. Determination of an appropriate cement plant site would be required.

Phase 4 – Site Remediation of the former stockpile locations will be required. However, low-cost, low-tech remediation technologies could be used such as cleaning out the pesticide storage buildings and restricting their future use to inert items only.

In conclusion, the NATO project to repack, centralize and analyze the pesticide stockpiles in Moldova progressed well. There were several delays on the project but the Moldovan MOD was able to find solutions to alleviate the problems. There is a need to complete the remaining two steps of the project to prevent additional damage to the pesticide stockpiles like the fire and vandalism at the relocation warehouses discussed above. In addition cost effective methods for the destruction of the pesticides and site remediation of the former stockpile locations will need to be chosen as funding will be required to complete these activities in a timely fashion.

ELIMINATION OF RISKS OF OBSOLETE PESTICIDES IN MOLDOVA, GEORGIA AND KYRGYZSTAN 2005-2008

Iordanca-Rodica IORDANOV[1], Sandra MOLENKAMP[2]

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Milieukontakt International is executing a project Elimination of risks of obsolete pesticides in Moldova, Georgia and Kyrgyzsta, 2005-2008 with financial support of the Dutch Ministry of Foreign Affairs and the Dutch Foundation DOEN, in cooperation with engineering company Tauw, the International HCH and Pesticides Association (IHPA) and the Dutch NGO Natuur en Milieu (Nature and Environment). The aim of this project is to repackage obsolete pesticides in the regions of Hincesti (Moldova), Kakheti (Georgia) and Osh (Kyrgyzstan). An important aspect of the project is the multi-stakeholder approach; Milieukontakt involves local experts and local citizens who are trained in taking inventory of pesticides stocks, risk analysis and in repackaging obsolete pesticides. A local working group (consisting of stakeholders from government, state institutions, NGOs, business, local citizens) coordinates and monitors all activities within their region, and raises awareness among local citizens of problems related to pesticides in the derelict storages near their houses.

Key-words: repackaging obsolete pesticides, public participation, multi stakeholder approach, local involvement, phyto remediation, sustainable agriculture.

Introduction to our organisation Milieukontakt International

Milieukontakt International is a Dutch organisation with twenty years experience in training, support and cooperation for a better environment. We are active around the world but mostly in Eastern Europe, Central Asia, the Balkans and the Caucasus.

Milieukontakt uses a three tier approach in implementation of its projects:

1. **building capacities:** strengthening networks, (N)GOs and working groups of local people using training, support and advice thereby building self-reliance and independence;
2. **involving citizens:** participative methodologies are employed to ensure maximum participation in solving environmental issues. Within our projects on Green Agenda and obsolete pesticides we always work according to a multi-stakeholder approach; and
3. **solving environmental problems.**

What do we work on? Our main topics are:

1. Elimination of risks of obsolete pesticides.
2. Green Agenda, a method for local sustainable development.
3. Effective environmental movements.
4. Knowledge management and knowledge sharing through ICT.
5. Training by MITT (Milieukontakt International Trainers' Team) to (environmental) organisations, (N)GOs and local citizens.
6. Integrated water management.

Save the penguin in Moldova

A few years ago Milieukontakt decided to help solve the risks of obsolete pesticides scattered all over countries of the former USSR because of the strong negative effects on environment and human health.

In the 1950-1990s an estimated total amount of 560,000 tones of pesticides were used in Moldova, including 22,000 tones of persistent organochlorinated compounds (OCPs). Pesticides use registered a peak in 1975-1985, but reduced dramatically over the last 10-12 years (from 38,300 tons in 1984 to some 2,800 tons in 2000, as active ingredient).

In 2004 we formulated a project proposal on eliminating risks of pesticides in three countries, together with Tauw, IHPA and the organisation Nature and Environment. Tauw helps us train local people on inventory of pesticides stocks, risk assessment and repackaging obsolete pesticides. IHPA gives advice about the activities within our project and about technical aspects related to obsolete pesticides. Milieukontakt also tries to look at possibilities for sustainable agriculture and integrated pesticides management together with NGO Nature and Environment. In 2007 we prepared the report *Opportunities for the realisation of sustainable food chains in Moldova*, and currently we are looking for possibilities to set up pilot projects on sustainable agriculture in Moldova and Georgia.

Many problems pertaining to obsolete pesticides are the result of a lack of awareness and interest of and money from local authorities and citizens. Until today many local citizens use building materials from old storages to make sheds or fences, or they sell obsolete pesticides to their neighbours who will use them in their small gardens.

The World Health Organisation estimated (WHO, 1986) that 1 million people are affected by insecticide poisoning every year and that 20 000 die as a result of being unaware of the risks involved in handling insecticides. Strong evidence suggests that POPs and other pesticides in the environment are associated with the following dangers to human health:

– Tumours and cancers;
– Reproductive failure and reproductive abnormalities in both men and women;
– Cognitive deficits including learning and behavioural disorders;
– Immune system deficiencies and disorders;
– Incidents of other specific diseases such as endometriosis and diabetes.

Ways of exposure to obsolete pesticides are numerous. The most obvious are: pesticide vapours, direct contact in or close to unprotected stores, contaminated soil are spread around by wind and vehicles and polluted surface- and groundwater.

Therefore Milieukontakt has been eager to involve local citizens and experts in solving the problems caused by obsolete pesticides, and to inform local people about the project and the dangers connected to the old storages and the pesticides in corroded barrels and broken bags. It has been our aim to solve the problem together with local people, realising of course that this problem already has global implications; residues of pesticides are found in penguins on the South Pole. By starting to solve problems on a local level with local people whose daily lives are influenced by the obsolete pesticides, we prevent greater damage to the environment on a global level.

What did we do in Moldova?

After consulting Moldovan ministries and NATO and Worldbank project staff, we set up our project in the Hincesti region. In June 2005, we started by organising a meeting with local people who were interested in solving problems related to obsolete pesticides in their region. After this a working group was created with specialists from environment, agriculture, plant protection, health, local administration and civil society**.**

This working group and the national project manager coordinated and monitored activities carried out within the project: organising public meetings, participating in trainings on inventory, risk assessment and repackaging, informing the local population and making publications, cooperating with the local government, arranging importing of UN approved materials, helping organise repackaging activities, monitoring of repackaging and storing processes, setting up cooperation with national projects and other projects on OP issues.

1. Local working group and international expert discussing at one of the sites

What are the results?

When all the POPs projects started in Moldova, the total amount of obsolete pesticides in all the destroyed storages was not known. Therefore we trained the local working group on doing an inventory. In total 98 tons of obsolete pesticides were found in the Hincesti district. All information gathered during the inventory were included in a database.

2. Repackaging in Hincesti region

In the summer of 2006, 108 tons of obsolete pesticides were repackaged in Hincesti according FAO standards. Of these activities and of activities in the months before the final repackaging, we made a documentary called *The Eliminator* in cooperation with AVE-film Moldova. The documentary is 50 minutes long and shows very well the hard work done by local people. Some unique old footage from the Soviet period shows the optimism about pesticides and the way pesticides were sprayed all over the agricultural fields in Moldova. The documentary has been distributed during several conferences, the HCH forum, during the Environment for Europe Ministerial Conference in Belgrade (October 2007) and was shown during an international environmental film festival in Armenia.

In addition, we would like to mention the following results: renovation of the central storage where all repacked pesticides in Hincesti were stored, the project was carried out by local people who were trained by an international expert on inventory taking, risk assessment and repackaging, public participation was guaranteed, an active network on pesticides issues exists, and the experience we gained in Moldova we are now using for our projects in Georgia and Kyrgyzstan. And finally; we also decided to start a pilot project on phyto remediation at a site in Hincesti. This decision was taken after meetings with local people during which they raised the question about what could be done with the old storages and how the soil at and around the storages could be used again.

Phyto remediation in Hincesti

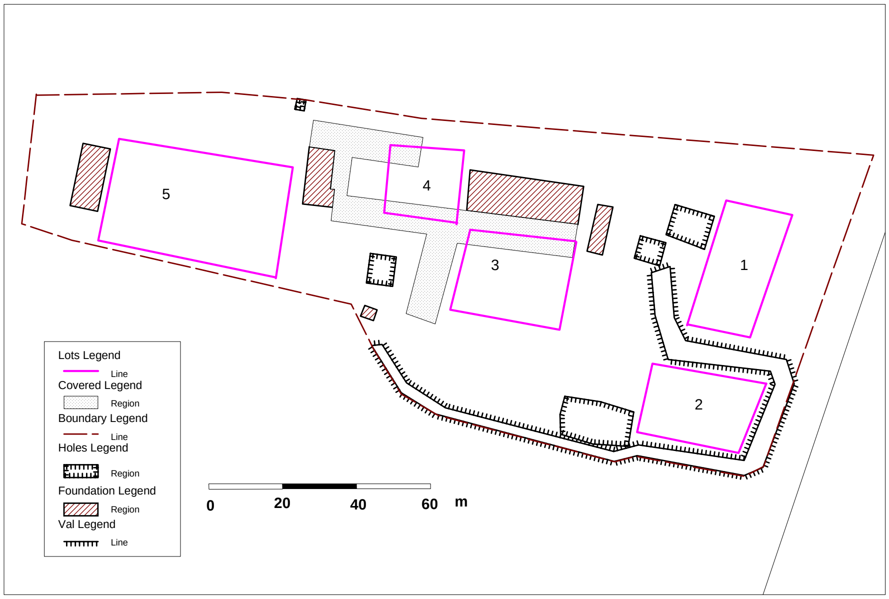
In January 2007, Milieukontakt started a pilot project on phyto remediation in the Hincesti region, in cooperation with a local farmer and Geolab: the Moldovan Geological State Institute.

The old site at Balceana was selected for the pilot project. During the HCH forum in Chisinau, Geolab held a presentation on the preliminary results of this project and during the 3rd day of the forum many of us visited this site.The Balceana site experiment is designed for the investigation of DDTs uptake by plants from the soil. Local plant species that were planted on the site are corn, zucchini, pumpkin, carrot and sorghum. Milieukontakt is continuing the pilot project in 2008, together with Geolab and the local farmer who is responsible for planting, harvesting and the fence around the site.

What's next?

In the spring of 2008, Milieukontakt and Tauw, in cooperation with local citizens, will repackage obsolete pesticides in Kakheti (Georgia) and Osh (Kyrgyzstan). At this moment a central storage is being built in Georgia and an Environmental Impact Assessment is being carried out in Osh. In 2008 we receive funding for carrying out a similar project in Ukraine (*Elimination of Risks of Obsolete Pesticides in Ukraine 2008-2010*). Since early 2008, Milieukontakt also receives funding from the Dutch Ministry of Environment and Spatial planning for the project O*bsolete Pesticides- a "Burning" Question*. In this project Milieukontakt –

together with IHPA and Nature&Environment- wants to look at alternatives for incineration of obsolete pesticides, and particularly we want to research some aspects of these alternatives related to environmental impact, costs, practical value, for which pesticides can they be used, and if these methods can be used on site. We are also looking into other possibilities for projects where Milieukontakt's role will be to involve local stakeholders and NGOs into the process of elimination of risks of obsolete pesticides.



3. Lay-out of phyto remediation plots at Balceana site, Hincesti region, Moldova

More information

If you would like to know more about our organisation or the projects that we carry out, please contact us at the e-mail addresses mentioned below. You can also contact us if you don't have a copy of our documentary *The Eliminators* but would like to receive one!

References:

1. J.Donner. Repackaging obsolete pesticides without involvement of local citizens/In Caution Dangerous Chemicals-Obsolete Pesticides (edited by W.S. Kuc), p.316-322, 2007.

2. O.Bogdevich. Interim report of the project "Elimination of acute risks of obsolete pesticides, component phyto remediation", June 2007.

3. National implementation Plan for the Stockholm Convention on Persistent Organic Pollutants, Chisinau, 2004.

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POPs PESTICIDES MANAGEMENT IN THE REPUBLIC OF BELARUS IN ACCORDANCE WITH THE NIP FOR THE STOCKHOLM CONVENTION

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In accordance with Decree of the President of the Republic of Belarus No. 594 "On Belarus' Accession to the Stockholm Convention on Persistent Organic Pollutants" of 26 December 2003 (the National Register of Laws and Regulations of the Republic of Belarus, 2004, No. 1, 1/5208), the Republic of Belarus consented to be bound by the Stockholm Convention on Persistent Organic Pollutants.

The National Plan of the Republic of Belarus for the Implementation of its Obligations under the Stockholm Convention on Persistent Organic Pollutants for 2007-2010 and until 2028 (the National Plan) has been developed in order to define effective measures and concrete actions aimed at addressing the problem of persistent organic pollutants in the Republic of Belarus and to implement its obligations under this Convention. In order to make the National Plan a legally binding document at the national level it was approved by Decree of the President of the Republic of Belarus No. 271 of June 12, 2007. The major objective of the National Plan is to set priorities in addressing the problem of persistent organic pollutants (POPs) in Belarus for 2007-2010 and until 2028 as well as to define the priority implementation activities for 2007-2010. At present POPs pesticides management in the Republic of Belarus is regulated by the National Plan as well as by other legal documents related to the POPs management.

Key Words: Stockholm Convention, persistent organic pollutants, pesticides, National Implementation Plan, obsolete pesticides landfills, prevention of pesticides migration

The nature of the POPs pesticides issue and their impact on the environment and people's health in Belarus are similar to that found elsewhere in the republics of the Former Soviet Union (FSU), particularly European Russia and Ukraine that share a similar history of agricultural and industrial development. POPs pesticides have never been produced in Belarus, the import or use of POPs pesticides in any new applications had been banned by the 1980s along with other countries in the FSU. However, POPs pesticides had been used historically. DDT was the most popular POPs pesticide in common use at one time although aldrin, heptachlor, hexachlorobenzene (HCB), were also used to a limited extent. Additionally, the usage of hexachlorocyclohexane (HCH) or lindane occurred. This pesticide is already controlled under the 1998 Protocol to the 1979 Convention on Trans-boundary Air Pollution on Persistent Organic Pollutants and represents one the of the potential candidates to the list of the POPs regulated by the Stockholm Convention.

The National Plan of the Republic of Belarus for the Implementation of its Obligations under the Stockholm Convention on Persistent Organic Pollutants for the period of 2007-2010 and until 2028 (National Plan) was approved by Decree of the President of the Republic of Belarus No. 271 of June 12, 2007. This document establishes the priority areas of POPs management in Belarus as well as POPs pesticides management. Among the priorities relating to POPs pesticides are the following:

- improvement of the Belarusian legislation, institutional and regulatory frameworks for the management of POPs pesticides;
- environmentally sound storage and disposal of the existing wastes containing POPs pesticides;
- identification, assessment and clean up of POPs pesticides contaminated sites and remediation of the affected environment.

As of 1 January 2007, 6558 tons of obsolete pesticides were stockpiled in storehouses and burial sites in Belarus including 718 tons of DDT, which is included in the list of persistent organic pollutants controlled by the Stockholm Convention. 3.372 tons of DDT are stored in storehouses, 714.53 tons – in landfills. 2007.9 tons of unidentified obsolete pesticides mixtures are stockpiled in the storehouses; 749.699 tons of obsolete pesticides mixtures have been buried.

Unidentified obsolete pesticides mixtures are considered as potentially containing persistent organic pollutants.

In the framework of the implementation of the GEF/ World Bank project "Enabling activities related to the implementation of the Stockholm Convention on persistent organic pollutants in the Republic of Belarus" about 144 samples of unidentified mixtures of obsolete pesticides were analyzed. These samples were taken at the stockpiles where the largest quantities of unidentified mixtures are stored; these are the storehouses of the three regions of the republic: the Vitebsk, Grodno and Minsk regions.

In the Minsk region the biggest amount of the mixtures of obsolete pesticides is concentrated in the storehouses of the Slutsk district – 50.2 tons, Borisov district – 24.839 tons, Dzerzhinsk district – 19.423 tons, Kopyl district – 19.26 tons, Minsk district – 35.421 tons, Molodechno district 20.748 tons, and Starodorozhski district – 18.58 tons. There are 94 obsolete pesticides storehouses in the region all in all.

In the Grodno region all the stocks of obsolete pesticides are accumulated on the territory of eight districts: the Volkovyssk district – 239.544 tons, Voronovo district – 36.2 tons, Grodno district – 123.1 tons, Zelva district – 404.952 tons, Ivje district – 86.257 tons, Lida district – 42.536 tons, Novogrudok district – 218.399 tons, and Smorgon district – 211.453 tons. All in all there are 17 storehouses in the Grodno region.

The total amount of POPs pesticides in the Vitebsk region is 2.28 tons and 274.719 tons of the mixtures of obsolete pesticides are dispersed practically over all administrative districts of the Vitebsk region.

The results of the analysis of the samples taken at 14 biggest storehouses of the above mentioned regions revealed the presence of POPs pesticides in 35 samples out of 144, which comprises 24.3 % of the total number of samples. Hexachlorocyclohexane (HCH) was revealed in 55 samples, which makes 38 % of the total amount of the samples taken. The most frequent pesticide is heptachlor, it was found in 15 samples; aldrin was revealed in 10 samples; apart from that separate samples contained chlordane, endrin, DDT and its metabolites.

The results of the analysis are shown in table 1.

Table 1. Results of the analysis of the samples taken from the biggest stokpiles of the mixtures of obsolete pesticides in the Minks, Grodno, and Vitebsk regions

Storehouse	**Pesticide and its maximum content in samples (g/kg)**											
	Aldrin	Heptachlor	Heptachlor epoxide	DDD	DDE	DDT	Chlordane	Endrin	α-HCH	β- HCH	γ- HCH	δ- HCH
Stockpile “Dubrovensky rajagroservice”		0,5	2,6						6,5		0,02	0,2
Stockpile “Verkhnedvinsky rajagroservice”		0,1	0,9						205	0,01		
Stockpile “Postavsky rajagroservice” (1)												
Stockpile “Postavsky rajagroservice” (2)			3,3									
Stockpile “Gorodoksky rajagropromsnab” (1)									228	17,8		4,5
Stockpile “Gorodoksky rajagropromsnab” (2)						0,2			506	65	0,2	38
Stockpile “Lepelsky rajagroservice”	0,1	0,2	0,6				2,7	0,2	119	11,3	0,4	6
Stockpile v. Leshchanka Novogrudok	1	7,8	1,4	0,03	0,06		2,4	0,05	26,4	0,03		

Storehouse	Pesticide and its maximum content in samples (g/kg)											
	Aldrin	Heptachlor	Heptachlor epoxide	DDD	DDE	DDT	Chlordane	Endrin	α-HCH	β- HCH	γ- HCH	δ- HCH
district												
Stockpiles “Tolochinsky rajagroservice”			0,1						339	24	53	18
Stockpile “Slutsky rajagroservice”	0,4	25,9	0,1		0,9	4,5			13,6		20,2	1,5
Stockpile “Zelvenskaya selkhozkhimija”	0,2		1,2		3			0,4	8,6		20,2	1,5
Stockpile “Ivjevskaya selkhoztekhnika”	0,32	6,5				0,34			0,97			
Stockpile “Starodorozhsky rajagroservice”									0,95	0,5		
Stockpile “Dzerzhinsky rajagroservice”												

As the data of the table illustrate, the POPs pesticides concentration in the samples ranges from 0.01 g/kg to 506 g/kg. These findings prove the assumption that unidentified mixtures of obsolete pesticides have to be treated as POPs-containing.

Apart from the storehouses of agricultural entities POPs obsolete pesticides are kept at the communal unitary enterprise «Facility for processing and burial of toxic industrial wastes of the Gomel region» and in seven landfills including three landfills in the Vitebsk region (the Verkhnedvinsk, Postavy and Gorodok landfills), one in the Brest region (in Gershony village), one in the Gomel region (the Petrikov landfill), one in the Grodno region (the Slonim landfill) and one in the Mogilev region (the Dribin landfill).

In most cases the conditions of storage of obsolete pesticides including POPs pesticides do not meet the environmental protection norms. The obsolete pesticides landfills were established in 1970s – early 1980s and their technical condition is not always secure; there is evidence of pesticide migration to the environment. The Dribin landfill represents a particular environmental hazard.

In accordance with the requirements set out in Article 6 of the Stockholm Convention, the Republic of Belarus shall take appropriate measures so that the stockpiles of POPs obsolete pesticides are handled, collected, transported and stored in an environmentally sound manner in order to prevent POPs releases to the environment. The country shall also ensure environmentally sound disposal of POPs pesticides in the future. The Stockholm Convention also provides for the development of appropriate strategies for identifying sites contaminated by chlororganic pesticides and remediation of those sites.

Belarus is undertaking measures to meet the abovementioned requirements set out in the Stockholm Convention.

The country has banned import, export and use of the pesticides listed in the Stockholm Convention; has established the requirements for recording, inventory, transportation, repackaging and storage of obsolete pesticides including POPs pesticides; occupational, labor and fire safety rules in the process of obsolete pesticides handling as well as the requirements for conducting monitoring of the environment in the districts where the obsolete pesticide storage facilities are located.

To prevent releases of persistent organic pollutants contained in the obsolete pesticides stockpiles to the environment, the obsolete pesticides are repackaged in order to ensure their long-term environmentally sound storage. 2006 tons of obsolete pesticides including DDT, unidentified chemicals and their mixtures were repackaged as of 1 January 2006. It is intended to complete repackaging of all stockpiles of the obsolete pesticides by the end 2007.

Strategy directions for POPs pesticides management include:

2007-2010:

- provision of environmentally sound storage of POPs pesticides;
- disposal of repackaged POPs pesticides;
- prevention and mitigation of the environmental impacts of the obsolete pesticides landfills.

2011-2020:

- regular inventory of the stockpiles of POPs obsolete pesticides to identify new stockpiles of POPs pesticides and their disposal sites;
- development and implementation of measures on environmentally sound handling of pesticides exhibiting the characteristics of persistent organic pollutants in case new pesticides are included in the list of persistent organic pollutants controlled by the Stockholm Convention;
- further elimination of the obsolete pesticide landfills;
- completion of the disposal of repackaged POPs pesticides;
- identification and clean up of the sites contaminated by POPs pesticides.

2021-2028:

- completion of clean up of the sites contaminated by POPs pesticides.

In the course of the development of the National Plan a number of particular activities relating to the POPs pesticides management in accordance with the provisions of the Stockholm Convention were suggested. The first activity presupposes completion of repackaging of POPs pesticides stockpiled at the temporary storehouses owned by organizations. The amount of financing is 150 million of Belarusian rubles. It is planned to have all obsolete pesticides including POPs pesticides repackaged by the end of the 2007. Nevertheless, it is worth mentioning that the repackaging of obsolete pesticides will go on together with the work on elimination of the obsolete pesticides landfills as the extracted pesticides will be repackaged and taken to the environmentally safe storage and then destruction. In this regard, the Republic of Belarus will need to attract additional external financing of repackaging activities as well as enhance its technical capacity.

One more activity to reduce the negative impact of POPs on the environment presupposes engineering and technical measures aimed at reduction of harmful environmental impacts of POPs pesticides stockpiled in burial places. As far as financial and technical capacity of the country does not allow expediting the total elimination of obsolete pesticides landfills in the Republic of Belarus it is very important to prevent any possibility of accidents relating to the releases of POPs pesticides to the environment from the landfills.

The most typical engineering solution for the landfills is prevention of pesticides migration to the groundwater. Usually groundwater in the area of obsolete pesticides landfills gets contaminated with chemicals due to infiltration of precipitates through the trenches with buried pesticides, their dilution and transport to the first aquifer from the ground surface. Prevention of precipitates infiltration into groundwater is ensured by construction of a special roof over the landfill and diversion of rain water out of the area of the landfill. This technical solution is effective for the territories where the maximum flood level of the groundwater lies 3-5 m below the bottom of the trenches.

The surface waters do not have direct contact with the buried chemicals. They may get contaminated only in case of groundwater discharge to the surface watercourses and reservoirs.

In the year 2007 it is planed to spend 247 million rubles on the implementation of technical measures that will help to reduce the migration of pesticides from the landfills to the environment.

The most costly and technically complicated activity relating to the reduction of the negative impact of POPs pesticides on the environment and people's health planned for 2007 is elimination of the Brest obsolete pesticides landfill. This landfill is different from the rest six landfills that are situated on the territory of the Republic of Belarus.

The Brest obsolete pesticides landfill is located in the south-west suburb of Brest between the villages of Mitki (north), Kotelnya-Boyarskaya (west and south-west) and Bernady (east and south-east).

The landfill is geomorphologically adjacent to the territory between the Zapadny Bug river and the Mukhavets river. The distance to the river-beds is 2.8 km to the west and 6.0 km to the north.

The obsolete pesticides are stored in the caponier of the fort marked with letter «3». According to the data of the Memorial «The Brest Fortress-Hero», this fort is a part of the second (outer) defense line of the Brest Fortress. Its construction was launched in 1912 and lasted until 1915 but was never completed. During the Second World War it was partly destroyed and until 1988 it was used as a disposal site for solid municipal wastes of Brest.

The caponier used for storage of pesticides is a concrete rectangular facility with sub-latitudinal orientta-tion. Its length is about 120 meters, width – 5 meters, height above the foundation is 4 meters. According to the staff of the Memorial, the design documents have been lost. Therefore, there are no reliable data on the structure of the foundation. It is believed that boulders fixed with binding materials were laid under the conc-rete foundation. There's a trapdoor going to the part of the caponier where no pesticides are stored.

In 1978 and 1988 all in all about 125 tons of 15 types of obsolete pesticides were buried in the caponier. Unknown pesticides and their mixtures make up about 70 per cent of the total amount.

The peculiarities of the landfill are conditioned by the following reasons:

1) pesticides were buried in a specific fortification facility (caponier) though built of concrete and on a stone and concrete foundation.

2) the caponier is built on the natural surface and the majority of pesticides are piled above the natural ground.

3) unlike other landfills, which are located in a dense and hardly accessible forests, the Brest landfill is lo-cated within an eminent plain close to hard-cover roads.

4) the landfill is located close to the settlements (0.5 km) and is surrounded by the villages of Bernady, Kotelnya-Boyarskaya and Mitki.

5) the site was also used for disposal of solid municipal wastes of Brest. By the time of its closure in 1988, it had accumulated a considerable amount (up to 6.0 meters) of different (most likely, not only munici-pal) wastes containing both organic and non-organic chemicals, which are well-soluble in water. The inven-tory data suggest that the Brest landfill contains up to 12.7 tons of unidentified mixtures of obsolete pestici-des, which can be potentially classified as POPs.

Taking into consideration these peculiarities a decision has been made to launch the first project on the obsolete pesticides landfill elimination mainly at the Brest landfill. First, it will be technically more feasible to extract the pesticides from the caponier than from underground. Second, the environmental hazard is ra-ther acute so the measures have to be taken immediately. The extracted chemicals will be repackaged and ta-ken to the specialized facility for the environmentally safe storage.

Any activity relating to the POPs pesticides management has to be regulated by the correspondent legal framework. In addition to the existing laws and regulations the National Plan presupposes elaboration and adoption of a number of regulatory documents, such as development of a regulation defining the procedure and terms of use, alienation, export and import of persistent organic pollutants, which will be approved by the Council of Ministers of the Republic of Belarus; development and enforcement of hygienic norms of the POPs pesticides content in food products and water. In terms of institutional capacity building one of the ac-tivities documented in the National Plan is development and maintenance of the POPs pesticides database, which will provide the stakeholders with the up-to-date information on the quantity and types of POPs pesti-cides, their storage sites and other details. The database will also facilitate the information exchange between the governmental and non-governmental organizations both inside the country and outside the country.

The National Plan delineates the strategic perspective for the POPs pesticides management until the year 2028. One of the most problematic issues for Belarus is destruction of the obsolete pesticides stockpiles. At present a decision has to be made whether to take all POPs pesticides to one of the facilities in Europe for en-vironmentally sound destruction or to build an installation on BAT principle in Belarus. There are pros and cons for both options therefore it is very important to keep the balance between environmental safety and economic efficiency and solve the problem of POPs pesticides stockpiles in Belarus with the least harm to people's health and the environment as well as with less expense.

NIP OF KYRGYZ REPUBLIC – RESULTS, BARRIERS AND OPPORTUNITIES

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The Republic is one of the 200 most important ecological regions on the planet due to its concentration of species diversity of flora and fauna. Thus, almost 2% of the world's flora and 3% of its fauna can be seen here, whereas the area of Kyrgyzstan is only 0.13% of the world's land mass. The Republic is located in a river formation zone and thus, any releases into trans-border rivers lead to irreversible effects, which in their turn can lead to disputes with neighbouring countries.

POP pesticides and PCBs have never been produced in the Kyrgyz Republic. According to results of the inventory 104, 683 kilos of obsolete pesticides were found and the total of POPs-pesticides comes to 20.68% of the total amount of the obsolete pesticides found. 1, 876.38 tons of pesticides including 1, 033.4 tons of POPs-pesticides were buried. Soil monitoring shows that the level of soil pollution with DDT is still high despite it was banned in 1970. POP pesticides were fond in glaciers and glacial lakes, high-mountain lake Son-Kul.

The results of PCB's inventory are: transformers – 19, 230 units; transformer oil – 14, 285.435 tons; transformer oil stocks – 139.662 tons; capacitors – 2, 373 units; capacitor oil – 24.407 tons.

In 2003 the total releases of dioxins were 30.5 g TEQ, and the greatest contribution is made by incinerating medical wastes – 7.01 g TEQ into air.

Of special concern was that the number of samples of breast milk containing DDT from 2002 – 2004 was almost double those in 1985. This could be linked to the fact that since 1995 cotton and tobacco growing has rapidly fallen and the population has started growing vegetables and fruit on the land.

NIP was approved by Government Resolution №_371-p of the Kyrgyz Republic dated 3rd July 2006

Key-words: NIP of Kyrgyz Republic, POP-pestisides**,** PCB, dioxins, medical wastes, diversity of flora and fauna**,** glaciers, glacial and high-mountain lakes**.**

Introduction

The Kyrgyz Republic is located in Central Asia between latitude 39° and 43° North and longitude 69° and 80° East. In the North, the republic boundaries the Republic of Kazakhstan, in the Southeast and East – the People's Republic of China, in the Southwest – the Republic of Tajikistan, and in the West – the Republic of Uzbekistan. Kyrgyzstan is a mountainous country with a large variety of landscapes, animals and plants, with really high mountain peaks, large glaciers and permanent snow. The republic is the main zone for forming the water resources for states of the Aral Sea area. Altitudes in the republic vary from 350 to 7, 439 metres and 94% of its land mass is over 1, 000 metres above sea level, of which 40% is higher than 3, 000 metres. The average altitude in Kyrgyzstan is 2, 750 m. Anthropogenic ecological systems occupy only 7% and the rest are inviolate or weakly affected natural ecological systems. The Republic is one of the 200 most important ecological regions on the planet due to its concentration of species diversity of flora and fauna. Thus, almost 2% of the world's flora and 3% of its fauna can be seen here, whereas the area of Kyrgyzstan is only 0.13% of the world's land mass.

Since gaining independence the Kyrgyz Republic has actively participated in the efforts of the international community to resolve environmental problems, both globally and locally. On May 16th 2002, Kyrgyz Republic signed the Stockholm Convention on persistent organic pollutants and ratified it on July 19th 2006, thus demonstrating its aspiration to cooperate with the international community. The National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants was developed under the supervision of the National Coordination Committee for the Stockholm Convention on POPs formed in accordance with Government of the Kyrgyz Republic Order № 688-p dated 14th November 2003. NIP was approved by Government Resolution №_371-p of the Kyrgyz Republic dated 3rd July 2006.

1. Analysis of the normative and legal base on chemicals and POPs management

The existing system of dividing chemical substances in the republic (pesticides, highly toxic substances, waste products from production and consumption, potentially toxic chemical substances, oil products, medicines, dumps and tailing dumps' wastes) proves the lack of clearly defined categories for specific substances. Some chemical substances fall into different categories. For example, pesticides with an expired shelf life including aldrin, dildrin, and prussic acid and its salts in tailing dumps are on the list of highly toxic substances and so on. As a result, various legal mechanisms can be applied to the same chemicals when regulating their use.

The basic weakness of the legal regulation in the POPs sector is the lack of a normative legal base. There are no any legal, organizational measures and technical opportunities for controlling and regulating unintentionally produced POPs. There are formal opportunities to control releases of unintentionally produced POPs based on the 'polluter pays' principle. However, the lack of a number of approved methods for calculating release volumes prevents control and registration because measurement of unintentionally produced POPs is expensive.

To a larger degree, requirements regarding chemical substances use are of a general ecological character predetermining the basic requirements to any type of economic activities regardless of the specific nature of using a considered substance or group of substances.

A unified government reporting system on both POPs and other toxic chemical substances is lacking and there is no inventory of substances that are identified as POPs. A unified information system on POPs and other toxic compounds management is lacking. Reducing the risks connected with POPs and other toxic compounds can be achieved by establishing interdepartmental and inter-sectoral partnerships when managing POPs and other toxic compounds.

2. Evaluation of problems regarding pesticides, including the list of POPs

POPs-pesticides have never been produced in the republic. POPs-pesticides were delivered centrally through Kirgizselhozhimiya (Kyrgyz Agricultural Chemistry) that previously was part of Souzselhozhimiya (Agricultural Chemistry Union), USSR. According to official data, POPs-pesticides have not been imported and then re-exported from the republic during the last 15 years. Their use in agriculture was prohibited over 20 years ago on the instructions of the former Ministry of Health of the USSR.

According to preliminary data, as a result of the inventory of places where Selhozhimiya (Agricultural Chemistry) stores were formerly located, former stores on collective farms, agricultural aviation airfields, 104, 683 kilos of obsolete pesticides were found including 30, 206 kilos in Osh region, 42, 386 kilos in Chui region, 9, 091 kilos in Issyk-Kul region, and 23, 000 kilos in Naryn region. According to the preliminary inventory, the total of POPs-pesticides in the republic comes to 20.68% of the total amount of the obsolete pesticides found.

1, 876.38 tons of pesticides including 1, 033.4 tons of POPs-pesticides were buried in the republic. Aldrin, HCCH, DDT and products of its decomposition, dieldrin and heptachlor have been found in the areas around these burial grounds. Illegal POPs-pesticides are smuggled into the country or stolen from old dumps and probably from stockpiles held on private farms.

Pesticides are stored in warehouses that do not meet safety requirements or have been partly destroyed; pesticide packaging is damaged and the pesticides are washed away by rain and pollute the adjacent land, surface and underground water. Construction materials from demolished or ruinous former stores are used to build residential houses, mosques and buildings for domestic animals; former stores are used for storing agricultural produce.

Former airfields and land adjacent to them are being used for housing and/or cultivating agricultural crops. Soil monitoring shows that the level of soil pollution with DDT and products of its decomposition is still high despite it being banned in 1970.

3. Assessment of PCB issues

PCBs have never been produced in the Kyrgyz Republic but could be brought into the country in electrotechnical equipment, transformer oil, paints and grease. There is no precise information on the import or export by quantity and types of electro-technical equipment, volumes and sorts of transformer oils, paints and other materials.

According to the results of the preliminary inventory in the Republic there are transformers – 19, 230 units; transformer oil – 14, 285.435 tons; transformer oil stocks – 139.662 tons; capacitors – 2, 373 units; capacitor oil – 24.407 tons.

There is no clear allocation of responsibilities among ministries and departments about PCB management.

There is no reliable information on the volumes of PCBs in working and decommissioned equipment, on equipment polluted with PCBs, on stockpiles of PCBs and polluted sites or on PCB content in foodstuffs. There has never been control of PCBs content in the environment due to the lack of the proper equipment. MAC levels of PCBs in water, soil, air and foodstuffs are not defined in law. There are no programmes for monitoring PCBs in the environment and, accordingly, no evaluation of adverse effects on human health and the environment.

4. Assessment of problems of unintentional POPs releases (PCDD/PCDF, PCB)

In 2003 the total releases of dioxins were 30.5 g TEQ, of which releases into the air accounted for 14.37 g TEQ or 47.11%, into water – 10.87 g TEQ or 35.63 %, into soil – 0.16 g TEQ or 0.52%, contamination of produce– 0.03 g TEQ or 0.1% and the residue was 5.08 g TEQ or 16.64 %.

The majority of releases are the result of combustion procedures, including domestic wastes, production of minerals, domestic heating, fires, electricity and heat generation and the greatest contribution is made by incinerating medical wastes – 7.01 g TEQ. The total volume of release of dioxins/furans varies proportionally to production activity, which is shown by the dynamics of changes in releases, when from 1990 - 1995 their volume fell by three times and then in the following 10 years, doubled. Measurements of dioxins/furans in the environment, human body and control over their sources have never been carried out for lack of an appropriate equipment.

5. Evaluation of the monitoring system in the Kyrgyz Republic

In the Kyrgyz Republic monitoring the pollution of the environment, foodstuffs and human body for persistent toxic substances began in the 1970s and was carried out by the Hydro-meteorological Service of the Republic and the Ministries of Agriculture and Healthcare.

The state of the technical infrastructure for POPs evaluation is poor. In general, due to the lack of funds for new equipment, it became outdated and worn out long ago and cannot provide the necessary level of measurements. Training and increasing the qualifications of analytical chemists and, in particular acquiring modern methods of physical-chemical analysis is the most critical problem in providing the chemical security of the Republic.

6. POPs impact upon public health and the environment

In spite of the fact that intensive use of POPs in Kyrgyzstan almost stopped in the late 1980's the presence of pesticide residues in the environment still represent a danger to public health. Higher incidences of infant mortality are noted and children under 14 are more often diagnosed with iron-deficiency anemia, viral hepatitis and acute respiratory viral infections.

Agricultural land. According to obtained data, from 1986 to 1992 out of 29.9 thousand hectares of test-sites, the area with DDT levels higher than MAC was 7.6 thousand hectares, or 25%. The most polluted (DDT and products of its decomposition) land in all examined oblasts is where cotton and tobacco are grown and in gardens.

Water and air. In the water of open reservoirs the most cases of exceeding the MAC of DDT was registered in 1993 in underground water in the Suzak rayon of Jalalabat oblast. It should be noted that number of checks on underground water for POPs levels has fallen significantly – in 2004 by 5 – 6 times compared to 1989-1990. Currently, underground spring water quality monitoring does not make it possible to really estimate the level of pollution because of the low number of observations.

Rivers. Kyrgyzstan is the only Central Asian country whose water resources are fully formed in its own territory. The Republic is located in a river formation zone and thus, any releases into trans-border rivers lead to irreversible effects, which in their turn can lead to disputes with neighbouring countries. In 2005 selective samples into drainage networks water for DDT and products of its decomposition's content was conducted in the area where the rivers in the Fergana and Talas Valleys are formed and the Issyk-Kul Lake basin. Water from the drainage networks is discharged into rivers and reservoirs and thus, can be a potential source of pollution. DDT and products of its decomposition were found in all the examined samples in quantities from trace amounts to many times MAC. Thus, rivers are a source of trans-border transfer of POPs-pesticides.

Son-Kul Lake. In the 1970's the land around Son-Kul high-mountain lake (3, 020 m) was used as pastures for livestock. In 1979 there was a plague of locusts there and pesticides including DDT and hexachlorocyclohexane were used for pest control. Later the pesticides were washed away by rain and snow into the small rivers that flow into the lake, leading to the mass death of fish and severely damaging the bio-diversity of the lake.

Glaciers and glacial lakes, located 2,500-4,000 m above sea level in Kyrgyzstan are sources of fresh water not only for the Republic but also for the Central Asian countries. A moraine lake whose water and soil samples were examined for pollution with POPs-pesticides is located near the Adygene Glacier in the Ala-Archa River basin on the north side of the Kyrgyz Ala-Too mountain ridge. It is very remote from agricultural land and pesticide stockpiles, which excludes the direct effect of economic activity upon the environment. Research into the glacial lake water showed DDT and products of its decomposition.

Foodstuffs. In general, analysis of laboratory data indicates that the levels of pollution with POPs-pesticides in food raw materials and foodstuffs had fallen from 2.6% in 1989 to 0.4% in 2004. Alongside this, levels of DDT and hexachlorocyclohexane in vegetable oil, meat, dairy products and eggs still exceed the norms by 1.5 – 2 times.

The area in the Republic where the content of DDT in foodstuffs has been most thoroughly studied is Osh oblast as it is the area where DDT, hexachlorocyclohexane, aldrin and heptachlor were most intensively used and has the highest rate of detection of these chemicals. Targeted research carried out in 2004 for POPs-pesticides' content in foodstuffs showed that traces were found in 18.8 % of dairy products, vegetable oil, 21.4% and meat products, 10.0%. DDT and products of its decomposition were found in: carrots, 69.9%, potatoes, 24% and onions, 34.8%. POPs-pesticides were found in 8.6% of the drinking water and open reservoir samples. It is important to note that POPs-pesticides are found in foodstuffs throughout the Republic.

Concentrations in the human body. Breast milk. In 2004 the Ministry of Health conducted research into levels of DDT and other POPs-pesticides in human breast milk. Of special concern was that the number of samples of breast milk containing DDT in the South of the Republic from 2002 – 2004 was almost double those in 1985. This could be linked to the fact that since 1995 cotton and tobacco growing has rapidly fallen in suburban areas of Osh and the population has started growing vegetables and fruit on the land.

In the breast milk of women from cotton-growing areas the simultaneous presence of two or more pesticides can be observed. The highest content of DDT and its metabolites, HCCH was noticed in breast milk of women from cotton- and tobacco-growing regions.

Problems of the impact of POPs on human health and the environment are aggravated by the absence of a reliable system of medical-ecological control and monitoring of the use of pesticides on farms and in imported agricultural products. At the same time due to lack of funds, sanitary and epidemiological research has been done patchily and not in full, which does not enable exact levels of the impact of individual POPs on human health to be determined.

7. Social assessment and activities of non-governmental organizations

In the course of preparing the NIP NGOs carried out social research into public awareness of POPs problems and as a result obtained data about the level of public awareness of POPs, of sources of information and opinions about the problem. Reasons for insufficient awareness of the public and representatives of groups whose activities are connected with POPs are the lack of information in the main mass media channels (television, radio, newspapers) and weak explanatory work by local authorities, ministries and departments of the Republic.

Within the frameworks of preparing the NIP a website of the project was designed **www.pops.kg**, where information about the project, results of the POPs inventory, an information storage and retrieval system about wastes and stockpiles of POPs in the Republic can be found.

8. Key national priorities of NIP

Thus, for the Kyrgyz Republic the most important actions are**:**

❖ **management of stockpiles (pesticides, PCBs) and wastes (POPs) in an environmentally safe manner. This includes:**

- making an additional inventory, repacking, collecting and transporting **POPs-pesticides** from revealed stockpiles to interim warehouses and storing them till their final destruction; eliminate burial grounds of pesticides in the Kochkor and Suzak regions.

- carry out a detailed inventory of **PCB-contaminated** equipment - transformers, capacitors, oils; develop a database; label all equipment; set up areas for holding, collecting and transporting PCB-materials; controlling the repair and oil changes of PCB-contaminated equipment; designing a plan for destroying PCB-contaminated equipment and oils;
- assessing **unintentional releases** and their impact on the environment in the two largest cities of the country (Bishkek and Osh); preparing a feasibility report (FR) on recycling medical wastes; develop a nationnal strategy on reducing releases as a result of burning fuel, domestic wastes and polluted plant residues of cotton and tobacco to heat houses in the countryside; developing an action plan to reduce or eliminate sources of unintentional POPs releases; promote BAT and BET;
- making additions and amendments to the legislation concerning **POPs management** in accordance with international standards; develop a full package of directive and normative documents; develop a POPs database; organize a monitoring and evaluation system; develop appropriate methods and improve the technical capabilities of laboratories; establish regional cooperation on POPs problems in Central Asia;

❖ **develop appropriate strategies for identifying POPs-contaminated sites and on-site remedial measures in an environmentally safe manner**;

❖ **public information, awareness and education**

❖ **scientific research, developments and monitoring of POPs and similar chemicals,** particularly, solving problems of trans-border movements of pollutants (glaciers, rivers, lakes) through regional cooperation with China, Kazakhstan, Tajikistan and Uzbekistan; hazard assessment and elaboration of united actions.

❖ **establish an inter-departmental coordinating committee on implementation of the Stockholm Convention's requirements and appoint its working body.**

9. Conclusion

The NIP includes tasks for strengthening the scientific and professional potential of the country, applying best available techniques and best environmental practices training specialists, adapting the most effective and environmentally sound methods of eliminating POPs, creating a centralized information system and monitoring and evaluation of the NIP implementation. It is proposed that the National Coordination Committee of Kyrgyz Republic will provides the Parties and the Secretariat of the Convention with regular information and reports on the implementation of the NIP and of problems of POPs at national level. The NIP includes cooperation with Central Asian countries on issues of the Convention. Reporting will be based on comparable data defined by the Convention Secretariat that will be the basis for the system of monitoring and evaluating the effectiveness of the NIP implementation in Kyrgyzstan.

The most critical issues are those connected with financing activities under the NIP. Along with providing a guaranteed allocation of budget funds it is necessary to seek new sources of funding. Due to the acute budget deficit it is important to actively attract investments and defining subjects for donor aid for the technical, information, scientific and professional improvement of national potential.

THE MAIN REGULATIONS OF THE UKRAINIAN NATIONAL IMPLEMENTATION PLAN FOR THE STOCKHOLM CONVENTION ON PERSISTENT ORGANIC POLLUTANTS: PROBLEMS AND WAYS OF THEIR SOLUTION

A.ANTONOV, A.GAMERA, V.DOUNYUSHKIN, E.LIGOSTAEVA

National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants (NIP) has been developed in the network of the project #GF/2732-03-4668 with participation of qualified specialists of a number of famous scientific establishments. The Institute of Occupational Health of the AMSU, L.Medved Institute of Ecological Hygiene and Toxicology of MHU, Institute of Technical Thermal Physics of the NASU, Council for studying productive forces of Ukraine of the NASU, etc. are among them. Representatives of central bodies of executive power (Ministry of Health, Ministry of Agrarian Policy, the State Statistics Committee, Ministry of Environment Protection and others), as well as non-governmental organizations ("Ecology. Woman. World", "Democracy and Development", "Green world", "Inmark – Information and Marketing" and others) took part in its development, too. The Plan contains concrete measures purposed to shortening or elimination of POPs and creation of preconditions for approval and realization of NIP in Ukraine. It foresees carrying out of activities purposed to implementation of the obligations according to the Stockholm Convention on POPs by Ukraine in accordance with the directions purposes and approximates cost of those are shown in table 1.

Activities foreseen by NIP

Table 1

Directions of the activities	Purposes of the activities	Approximate cost, mln. UAH
1. Strengthening of institutio-nal system and improvement of legislative base	Improvement of existing Ukrainian legislative and normative base by way of its bringing to compliance with the require-ments of the Stockholm Convention and Protocol on POPs as well as perfection, and ensuring mechanism of implementation of these requirements	**3.95**
2. Neutralization of stockpiled obsolete and banned pesticides as well as industrial wastes belonging to the POPs group	Reduction of influence of stockpiled obsolete and banned pestici-des as well as industrial wastes belonging to the POPs group upon population health and the environment by their stepwise neutralization by ecologically and economically acceptable methods	**360.28**
3. Neutralization / destructtion of PCBs-containing wastes and equipment	Realization of management of PCBs-containing equipment and waste using methods and technologies safe to human health and the environment	**484.952**
4. Reduction or elimination of releases of POPs from unin-tentional production	Reduction of harmful influence of POPs upon health of the population and the environment	**11.761**
5. Identification and management of territories polluted with POPs	Improvement of the system for control and management of contaminated territories including those polluted with POPs	**2.717**
6. Exchange with information on POPs among concerned parties, and increasing public awareness and education	Development of an efficient information exchange at the natio-nal, regional and international levels, and creation of me-chanisms for involving the major social groups in solving the problem and implementing the measures concerned with POPs	**22.038**
7. Development of the system of POPs monitoring in Ukraine	Improvement of the existing system for POPs monitoring in Ukraine in accordance with the requirements of the Stockholm Convention and the Protocol on POPs and supply of the state controlling bodies in the sphere of health and the environment protection with real data concerning content of POPs in the environmental objects, food products, and biological media for the purpose of effective protection of population health and the environment from harmful influence of POPs	**60.554**

8. Scientific research	Carrying out research and obtaining data for approval of decisions and planning of measures for reduction of POPs influence upon the environment and population health	**6.837**
Total, mln. UAH		**953.09**

Approximate expenses for neutralization of POPs revealed in Ukraine and remediation of the territories polluted with them

Table 2

Names of the objects to be neutralized	Revealed amount, tons	Approximate value of neutralization, mln. USD
Identified obsolete and banned POPs pesticides	2,019.2 (1,744 of DDT, 273.2 of HCCH, 1.5 of heptachlor, and 0.3 of HCB)	**6.0**
Not identified obsolete and banned POPs pesticides	18,582.0	**37.0 to 39.0**
Hexachlorobenzene – industrial waste	11,088	**22.0 to 25.0**
Total amount of chemical means for plants protection and industrial wastes ascribed to POPs	31,689.2	**70.0**
PCBs-containing capacitors (150,000 to 200,000 items)	9,000 to 12,000 (total mass of capacitors)	**27.0 to 36.0**
PCBs-containing transformers (1,500 to 3,000 items)	8,300 to 16,600 (total mass of transformers)	**13.5 to 27.0**
PCBs extracted from transformers	3,070 to 6,140	**7.7 to 15.3**
PCBs stored at storehouses	400 to 600	**1.1 to 1.5**
4,983 revealed sites for storage of obsolete pesticides polluted with POPs		**8.6**
PCBs leakages	4.148	**1.0 to 1.5**
PCBs releases	0.052	**0.2 to 0.3**
HCB releases	0.553	**0.4 to 0.5**

The Project collaborated in the network of informational exchange with other international ones. Project #P-169 "Management of Residual Agrarian Chemical Weed and Pest Killers and Neutralization of Obsolete Pesticides in Cherkasy and L'viv Regions", similar Project for NIP development in Kirghizia, Projects supported by Danish Agency for environment protection and others are among them.

NIP has been developed in accordance with the national strategy of sustainable development and programs purposed to harmonization of economical, environmental, and social aspects of the development.

State of handling obsolete pesticides and industrial wastes ascribed to the POPs group in Ukraine has been analyzed. It was determined that the following specific features are intrinsic to it:

- insufficient level of normative and lawful regulation, control, and monitoring of POPs;
- imperfection of the system of state accountability and POPs inventory;
- unavailability of systematic approach to determine the sites polluted with POPs as well as environmental objects, and remediation of the soils;
- unavailability of systematic monitoring of negative influence of POPs upon state of health of some categories of the population;
- availability of but a single plant for neutralization of POPs with a capacity of up to 500 tons per year;
- scantiness of chemical and analytical base as well as methodical base for determination of chemical substances ascribed to the POPs group, and insufficient number of accredited laboratories as well as qualified specialists in the sphere;
- imperfection of informational policy as to properties and specific features on negative influence of POPs upon the environment and human health;
- insufficient level on scientific knowledge, scantiness of complex scientific researches of problems concerned with handling POPs and technologies of their neutralization acceptable from ecological view-point *and*
- insufficient level of financing measures purposed to realization of measures concerned with handling of POPs and solution of the problem of neutralization of their stockpiled reserves.

At the same time, the main problem concerned with NIP implementation is ensuring consolidation of financial resources from the direction of Ukraine and international financial support.

NATIONAL IMPLEMENTATION PLAN FOR THE STOCKHOLM CONVENTION ON POPS OF THE RUSSIAN FEDERATION

Elena PERSHINA

Centre for International Projects, Moscow, Russian Federation

The Russian Federation signed the Stockholm Convention on POPs on May 22, 2002.

To implement obligations envisaged by the present Convention (Article 7), the Russian Federation started the development of the National Implementation Plan (NIP), which main objective is protection of human health and the environment from adverse impact of persistent organic pollutants (POPs).

NIP is pointed to:

- strengthen the human resource and institutional capacity of the Russian Federation for the sound management of POPs;
- strengthen the Russian Federation's policy and regulatory framework to facilitate the environmentally sound management of POPs and other chemicals;
- provide strategies, action plans and measures likely to lead to the reduction of POPs chemicals production and use and, where possible, the elimination of their release to the environment.

Within the Russian Government, the national head organization responsible for implementation of international environmental protection agreements, including the Stockholm Convention, is the Ministry of Natural Resources (MNR) of the Russian Federation. MNR is the leading implementing and co-ordinating agency responsible for activities aimed at developing the NIP.

The MNR has assigned the Centre for International Projects (CIP), Moscow, to be the National Focal Point (NFP) (with the domestic title of National Co-ordinating Centre – NCC) for the Stockholm Convention on POPs and to be the executing organization for this Project.

NIP preparation and implementation structure was developed considering the scale and complexity of situation existing in the Russian Federation. Taking into account the scope of the country, as well as work amount, which is necessary to implement to provide implementation of the Stockholm Convention requirements, the Russian Federation preferred to elaborate its NIP in line with the GEF requirements using full cycle envisaged for the GEF full-size project. This means that NIP development is conducted in three stages.

1. PDF-A: **Preliminary determination and assessment of requirements for the development of the National Implementation Plan.** This stage was completed in 2004.

In order to facilitate coordination among stakeholders with responsibilities for aspects of the Stockholm Convention, the MNR established an IAC.

Governmental agencies and services as well as representatives of industrial associations and enterprises, research institutions, academia, environmental NGOs and community representatives from "hot spot" locations also contribute to IAC and its Working Group activities.

2. PDF-B: **Capacity building to implement the Stockholm Convention on POPs and develop a National Implementation Plan** (2006-2007), that will have as its principal objectives the development of the NIP and capacity building at Federal and regional levels in order to implement priority actions, namely.

- collation and preliminary assessment of information on institutional, technical and financial aspects of existing infrastructure and capacities of executive authorities and their regional branches, industry, research and educational institutions and NGOs for the environmentally sound management of POPs;
- collation and preliminary assessment of information on the efficiency of existing legislation and regulatory mechanisms with a view of their adaptation for implementation of the future NIP;
- collation and preliminary assessment of information on POPs monitoring system, research and chemical analytical control, including accredited laboratories;
- collating and initial review of the following POPs inventory data:

- production, use, import and export of chemicals listed in Annexes A and B to the Stockholm Convention;
- stocks of POPs chemicals, hazardous wastes, landfills and burials that potentially contain POPs,

including POPs pesticides;

- types of PCB use, PCB containing equipment, storage and destruction sites;
- existing and future potential releases of POPs listed in Annex C to the Stockholm Convention;

- initial review of sources of POPs releases in contaminated sites and discussions on the problem with representatives of industry and local authorities;
- exploring possibilities of use of regional PRTRs for developing preliminary POPs inventory in pilot regions;
- preliminary assessment of POPs impact on human health and the environment;
- setting of priorities for further action aimed at reduction of POPs risks;
- submission to the IAC, federal and regional authorities of a report setting out recommendations for activities to be included in the Project Brief.

In the course of the Activity implementation, mechanisms of co-ordination among major stakeholders will be established; key elements of the future NIP will be identified; sources and methods of funding of the full-sized Project will be determined and secured.

3. a full-sized project – development of the **NIP for the Russian Federation** – designed for two years.

NIP will combine and complement existing efforts of the Russian Government, GEF and other organizations aimed at finding solutions for the POPs problem in the country and in the region. It is likely to have a significant impact at global, regional and national levels, *per se*. The Project will also allow priorities to be set for planning future activities to strengthen the capacity of Russia to comply with the Stockholm Convention.

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IMPLEMENTATION OF THE STOCKHOLM CONVENTION PROVISIONS AND ACTIVITIES TOWARDS REDUCTION AND ELIMINATION OF POPS IN THE REPUBLIC OF MACEDONIA

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POPs Unit/Ministry of Environment and Physical Planning Republic of Macedonia

*The Republic of Macedonia has ratified the Stockholm Convention on POPs (2004) and undertakes all responsibilities and obligations of the treaty. The Ministry of Environment and Physical Planning (MoEPP) - POPs Unit prepared the "National Implementation Plan (NIP) on Reduction and Elimination of POPs" through the GEF project, and the document was adopted by the Government in February, 2005. Following the recommendations identified within the NIP action plans, the MoEPP/POPs Unit actively participates in various projects in order to reduce or eliminate the presence of POP chemicals in the country. One of the projects was the Component IV of the "Energy Efficient Distribution Program" financed by the Swiss State Secretariat for Economic Affairs (**seco**). In the project, the PCB containing low voltage capacitors originating from the National electric distribution network are being dismantled, packed and transported to the interim storage prior to final shipment to Switzerland for disposal in the incineration facility. The other successfully done activity supported by the Swiss Government, was the removal of obsolete pesticides from the Public Health Department (PHD), where approx. 4000 kg of «Fumigant Cyclone B», «Methyl-bromide» and «Organochlorine Pesticide» obsolete stockpiles were taken out. The Republic of Macedonia is facing with an additional problem with huge quantities (app 35.000 tones) of obsolete stocks of technical mixture of HCH (α, β, δ) stored in the Organic Chemicals factory "OHIS". Some scientific findings indicate the presence of these chemicals in the younger population in the country. Thus, the MoEPP/POPs Unit is actively involved in the process of negotiations with the local and international institutions to support the Republic of Macedonia for final elimination of these stocks.*

Key words: POP chemicals, hazardous, obsolete pesticides, disposal, removal, reduction, elimination, HCH.

Introduction

The Republic of Macedonia is a mountainous country with many lowlands, located in the center of the Balkan Peninsula.(40-42" north latitude and 23-20' east latitude) with a total area of 25, 713 km^2 and population of 2,046,209.

The average altitude of the whole territory is 850 meters. According to the Spatial Plan of the Country, 1.9% of the territory is covered by water (lakes), 19.1% are Plains and valleys, and the biggest parts of 79% are hills and mountains. The climate in Macedonia is diverse. In the southern part of the country it is altered Mediterranean, in the central and northern areas it is mild continental and on high mountains - mountainous.

Since 1991, the Republic of Macedonia is an independent country with economy in transition with a status of member candidate of EU.

In the field of handling and managing persistent organic pollutants (POPs), Macedonia is a signatory to the following international conventions:

– Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal;

– Aarhus Convention on Access to Information, Public Participation in Decision-making and Access to Justice in Environmental Matters;

– Stockholm Convention on Persistent Organic Pollutants (POPs);

– ESPO Convention on Environmental Impact Assessment in a Transboundary Context,

– Kiev Protocol for Strategic Environmental Assessment and also is in a phase of preparation of initiative for Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade.

The National Environmental Legal framework is developed through the Law on the Environment. It lays the groundwork for implementation of EU legislation on transposition of Access to Environmental Information, Strategic Environmental Assessment of certain Strategies, Plans and Programs. Environmental Impact Assessment of certain projects, and Integrated Pollution Prevention and Control are also referred to in this law. The Macedonian framework environmental legislation is further developed by the Law on the Quality of the Ambient Air, Law on Waters, Law on Waste Management and Law on Nature Protection. The Macedonian framework environmental legislation fully complies with general features of the Stockholm Convention.

The national economy sectors, which are potential producers of POPs in Macedonia, have a potential for comparatively high formation and release of these chemicals in accordance with the Annex C to the Stockholm Convention. These sources are as follows:

- Agricultural production
- Textile industry
- Metallurgical industry-ferrous and non-ferrous
- Electric power plants and heating plants
- Chemical production – unintentional POPs production.
- Open burning of wastes including landfills

Implementation of the Stockholm Convention in the Republic of Macedonia

The Republic of Macedonia has signed the Stockholm Convention on POPs in May 2001, ratified it in March, 2004 and undertakes all responsibilities and obligations of the treaty. The Ministry of Environment and Physical Planning/POPs Unit prepared the National Implementation Plan (NIP) on Reduction and Elimination of POPs" through implementation of the GEF project "Enabling activities to facilitate early action on the implementation of the Stockholm Convention on POPs" The document was adopted by the Government of the Republic of Macedonia in February 2005. According to the results obtained from the preliminary inventories on POPs carried out in the frames of the initial GEF Enabling activities project 13 priorities were identified as follows:

1. Detailed inventory of POPs chemicals.
2. Establishment of a National POPs Center.
3. Inventory of “hot spots”.
4. Preventing uncontrolled waste combustion.
5. PCB/OCP containing waste management.
6. Preparation of new and amendment of existing legislation.
7. Monitoring of POPs.
8. Providing necessary equipment for and training on POPs monitoring.
9. Public awareness and education.
10. Evaluation of adverse effects on human health.
11. Monitoring of POPs bioaccumulation in living organisms.
12. Measures for the reduction of dioxin and furan emission.

a) Promotion of the use of unleaded fuels;
b) Adoption of principles of BAT (best available techniques in the industry);
c) Safe handling;

13. Control of PAHs.

(In Macedonia large quantities of technical waste (HCH) are stored that need to be solved in a proper manner. Although it is not listed in the Stockholm Convection annexes, it is also treated as a priority in order to find a prompt solution for this waste.)

According to the above mentioned priorities, 17 action plans were determined in the NIP. Within each of the action plans the specific milestones are given and under the optimal conditions, both institutional and financial, for implementation of the NIP the major milestone would be the year 2010 for phasing out of PCBs and the year 2015 for remediation of contaminated hot spots in the country.

Following the recommendations identified within the NIP action plans, the MoEPP/POPs Unit actively participates in various projects and activities towards reduction or elimination of POPs chemicals in the country, such as:

– Inventory of PCB and PCB contaminated equipment (Seco).
– Removal of organochlorine pesticides, MeBr and Cyclone B.
– Awareness raising activities (National Awareness Raising Program, Seco).
– Macedonia as a member of the Regional monitoring network is involved and coordinates the monitoring of PCBs, OCPs, and PAHs in the country with passive samplers - CEECsPOPs Centre - first regional project PAS_CEECs_II_2007.
– Initial activities (negotiations) of the POPs Unit/MoEPP with UNIDO’s assistance related to solving the problem with Lindane stockpiles in OHIS, Skopje.

The first project in the Post NIP period was the Component IV of the “Energy Efficient Distribution Program” financed by the Swiss State Secretariat for Economic Affairs (**seco**). In the project, the PCB containing low voltage capacitors originating from the National Electric Distribution Network (ESM) (app 40 tones of PCB waste) are being dismantled, packed and transported to the interim storage prior to final shipment to Switzerland for disposal in the incineration facility.

Picture 1. Interim storage of PCB equipment

Picture 2. Loading of containers with PCB waste

The other successfully finished project supported by the Swiss Government, was the Removal of obsolete pesticides from the Public Health Department (PHD), where approx. 4000 kg of «Organochlorine Pesticide» (Pic.3), «Fumigant Cyclone B» and «Methyl-bromide»(Pic 4,5,6) obsolete stockpiles were repacked, transported and disposed of in an environmentally sound manner.

Picture 3. Obsolete stocks of Organochlorine pesticides

Picture 4. Organochlorine pesticides

Picture 5. MeBR and Cyclone B

Picture 6. Repacking of Cyclone B

Problem with HCH stockpile in Ohis Skopje

The Republic of Macedonia is facing with an additional problem with huge quantities (app 35.000 tones) of obsolete stocks of technical mixture of HCH (α, β, δ) stored for more than 30 years in the Organic Chemicals factory "OHIS". The location is identified among the four Industrial Hot spots in the country. *OHIS' produced lindane in the period between 1964-1977, producing a quantity of up to 30,000t; precisely 200t/y product gamma lindane in addition to 1800 t/y waste of AlfA, Beta, Delta lindane.*

It is prudent to note that the dumpsite of lindane, alfa, beta and delta isomers is a concrete pool with a bottom that is not properly protected. It is suspected that there is a leakage of HCH and other POPs for a prolonged period of time in the underground soil and underground water.The discharges include alpha, beta, gamma and delta – BHC solid waste stored in a 'temporary' site for over 30 years and the waste amounts to 25-30 000 t Alfa and Beta Isomers. Most of the losses indicate leaching by the rainfalls and leakage through the collapsed or eroded concrete pool's bottom, which is used for BHC discharge. The waste adds to 3000t Delta isomer. A bio-accumulation factor is present; the leakage of HCH in ground water contaminated Vardar river empties into the Mediterranean Sea. This contamination is proved by investigation of the ground water. Nonetheless, bio-concentration in the flora and fauna of the river Vardar has still not been examined.

Medical studies have shown that there is evidence of antiandrogenic effects (cryptorchidism, atrophy of the testes, lower androgen levels in the blood), estrogenic effects (breast carcinoma). Malformation in newborns could also be caused by exposure to lindane. Thus, the MoEPP/POPs Unit is actively involved in the ongoing process of negotiations with the local and international institutions to support the Republic of Macedonia for final elimination of these stockpiles.

Picture 5. Alfa and beta HCH isomers storage

Picture 6. Delta HCH isomers storage

Conclusion

Based on the documents presented, such as the international obligations of the Republic of Macedonia (EU accession), signed and ratified international conventions, adopted legislation and approximation to the EU legislation, and on the basis of the prepared "National Implementation Plan on reduction and elimination of Persistent Organic Pollutants (POPs) in the Republic of Macedonia" adopted by the Government, the initial steps towards the implementation of the Stockholm Convention are fulfilled. The Republic of Macedonia is working on the Post NIP activities according to the preliminary POPs inventory, identified priorities and action plans in the NIP. During the activities undertaken in the previous period (2002-2007) Macedonia was facing with a lack of financial and human resources, lack of laboratory capacities and awareness among the relevant stakeholders and the general population, but as a country pioneer in the region gained a great experience in POPs management. Thus, the Republic of Macedonia is deeply interested and also able to contribute to the global action for reduction and elimination of POPs but due to limited financial resources, only with the permanent support and assistance by the international community. The upcoming and already approved projects related to POPs, PCBs and chemicals in general, illustrate the commitment on both sides to develop good chemicals and waste management system in the country.

References:

1. National Implementation Plan on Reduction and Elimination of the Persistent Organic Pollutants in the Republic of Macedonia POPs (2004).
2. Law on Environment, (Official Gazette of the RM, No. 24/07).
3. Law on waste management (Official Gazette No.68,71/2004).
4. Law on waters (Official Gazette No.2004).
5. Regulation on disposal of PCBs and PCTs (Official Gazette of the RM No.48/07).
6. Regulation on the disposal of waste oils.
7. Stockholm Convention (SC) (2001). Stockholm Convention on persistent organic pollutants. http://www.pops.int/.
8. Development Of Remediation Plans With Financial Requirements For Elimination Of Industrial Hotspots (Europeaid/123674/D/Ser/Mk) Inception Report -Final Version (April 2007).
9. Prof. Svetomir Hadzi Jordanov & Josif Tanevski – 'Pharmachem' consulting, Skopje, Republic of Macedonia.
10. Prof. Mirjana Kocova, MD, PhD; Pediatric Clinic, Medical Faculty University Cyril & Methodius-Skopje.

BETTER SYSTEMS FOR BETTER MANAGEMENT OF PESTICIDES IN USE AND PESTICIDE WASTE

Mark DAVIS

Prevention and Disposal of Obsolete Pesticides, FAO, Rome

The global volume of pesticides sold and used is small compared to other industrial chemicals. Nevertheless pesticides are designed to disrupt biological systems, are used by more individuals who are generally untrained, and they are distributed more widely and dispersed over vast areas of land. As a result much experience has been gained in the control and management of pesticides that can benefit chemicals management in other sectors. FAO is mandated to help countries develop and implement tools to manage pesticides. As such it has developed and revised the *International Code of Conduct on the Distribution and Use of Pesticides*, produces technical guidelines on implementation of specific aspects of the *Code*, jointly with FAO runs the *Joint Meeting on Pesticides Residues* and *Joint Meeting on Pesticides Standards*, jointly with UNEP runs the Secretariat for the *Rotterdam Convention*, operates the global Obsolete Pesticides Programme that also provides the Technical Support Unit to the Africa Stockpiles Programme, runs a programme to support improved policy and legislation for pesticides and links with other services of FAO dealing with crop protection, migratory pest monitoring and control, natural resource management, food quality and others.

A number of recent developments in the FAO approach to pesticide management and from the obsolete pesticides programme have evolved in response to demand from countries and experience gained by field work.

Integrated life cycle management approach to pesticides management

The *International Code of Conduct on the Distribution and Use of Pesticides* lays out recommendations on how each stage in the life cycle of a pesticidal product should ideally be managed. Over 12 Articles, the Code addresses the following issues:

Article 1. Objectives of the Code
Article 2. Terms and definitions
Article 3. Pesticide management
Article 4. Testing of pesticides
Article 5. Reducing health and environmental risks
Article 6. Regulatory and technical requirements
Article 7. Availability and use
Article 8. Distribution and trade
Article 9. Information exchange
Article 10. Labelling, packaging, storage and disposal
Article 11. Advertising
Article 12. Monitoring and observance of the Code

Interestingly the Code is not a legally binding instrument or Convention, but is an entirely voluntary scheme which has the unanimous endorsement of all 192 FAO Member States, the private sector including pesticide manufacturers and NGOs including ‘anti-pesticide’ groups.

Technical guidelines have been prepared to expand on and support the implementation of various aspects of the Code, and traditionally FAO and other organizations have guided and assisted countries in addressing specific issues. In the main, however, the Code has been promoted as a policy tool.

In response to demand from countries and the expansion in interest in chemicals management, a field programme to support comprehensive implementation of the Code is being developed by FAO. Recognizing that the needs on countries will differ, depending on their relative strengths and weaknesses, the programme will start with a comprehensive gap analysis to identify areas of greatest need for intervention.

It is crucial that the analysis includes as wide a range of stakeholders as possible in recognition of the vital roles each group of stakeholders plays in implementation of the Code. Farmers, for example, as users of pesticides, have a unique understanding of the realities of pesticide use, reading and understanding labels, responding to advertising, access to advice and retailers, personal and environmental protection, container management, and other real world issues. NGOs often play unique roles in educating and informing the public and pesticide users; the pesticide manufacturers, importers, distributors and retailers are best placed to understand their respective components in the life cycle of pesticides, and governments are responsible for regulation and enforcement, monitoring of health and the environment, health care and are often, but not uniquely responsible for advice to farmers, waste management and other important aspects.

The gap analysis will identify potential entry points or areas for intervention around which projects or programmes can be developed. An important example is the identification of obsolete pesticide stockpiles as an issue governments would like to address with urgency. Further gap analysis generally reveals that some of the causes of obsolete pesticide accumulation can and should also be addressed. These may include import controls, pesticide quality control, distribution systems, storage, and container management as well as obsolete product disposal.

The analysis leads to the development and implementation of a comprehensive capacity building programme designed to address several if not all identified weaknesses. Disposal of obsolete pesticide stockpiles therefore becomes a component in a wider package of activities designed to reduce health and environmental risks from pesticides throughout their life cycle.

Obsolete Pesticides Management System (OPMS)

OPMS is a computer based system designed to gather a comprehensive set of data on obsolete pesticides, their location and storage conditions and the environment around their point of storage. Once entered into the system, this data can be manipulated in various ways to provide outputs that assist in planning cleanup operations, costing and fundraising for cleanup operations and developing a better understanding of why the stockpiles were created.

Planning for cleanup is supported primarily by the site specific risk assessments produced by OPMS. These are generated by a calculation of the risk factor associated with the pesticides held in the store plotted against the risk factor of the store itself in the environment. The pesticide risk factor (Fp) takes account of the toxicity of each products, its quantity and condition. The Environment risk factor (Fe) takes account of the condition of the store and its proximity to sensitive environmental situations such as water, people, crops etc. The risk assessments can clearly help to identify the highest risk locations where attentions should be focused as a priority.

Information about the quantity and types of pesticides can help in calculating container and equipment needs for repackaging, transport and ultimately destruction plans. Additionally, information about the precise products in stores, including manufacturer and supplier information can help in fundraising efforts by approaching suppliers (producers or donors) for assistance in disposing of their obsolete products.

OPMS is currently deployed in countries participating in the Africa Stockpiles Programme Phase 1 and will be disseminated further as new projects develop. Other organizations working on obsolete pesticide projects are showing interest in being trained in its use and accessing the system for use in their projects, indicating that this may become the standard in obsolete pesticide inventory taking. This is a step that would be of benefit to everyone, in particular the countries and their populations who are seeking quick, efficient and effective solutions to their obsolete pesticide problems.

More information can be found at www.fao.org/ag/obstocks.html

Pesticide Stock Management System (PSMS)

The Pesticide Stock Management System (PSMS) has been developed to help countries affected by gregarious locust outbreaks to manage their very large stocks of pesticides that are generated over very short periods in emergency situations. The major driver for this development was the accumulation of 8 million litres of pesticides in the countries of western and northern Africa affected by the desert locust swarms of 2003-5. Many of these countries had already benefited from projects to eliminate obsolete pesticides and some are currently implementing such projects. It was therefore imperative that the creation of new obsolete pesticide stocks be prevented in these countries; otherwise previous efforts would be largely wasted.

FAO worked closely with country teams and other linked initiatives such as the World Bank African Emergency Locust Programme (AELP) to identify existing stocks of locust control pesticides and their locations. Action was taken to centralise these stocks as far as possible. In late 2006 teams from each country were trained to sample products in stock and a programme was launched to collect samples and send them to an accredited laboratory for analysis. This analysis was designed to determine the quality of pesticides in stock and determine whether they could still be used and what their remaining shelf life would be. In this way it was possible to ensure that product closer to their expiry either by age or quality, should be used first.

The need for a tracking system for pesticides was clearly identified, and efforts were put into developing a robust computer based system that all countries could use. FAO had already put much effort into developing the Obsolete Pesticides Management System (OPMS) and it was a short step to adapt this system for use as a tracking system for pesticides still in use.

The tool used for identifying and tracking individual pesticide containers is the bar-code, printed onto chemical and weather resistant labels. Bar code readers are widely available and easily held at each pesticide storage point for recording the arrival and departure of pesticides. In the absence of reliable internet access or WANs it was decided to resort to a paper based system to track the movement of products. All data is fed back to a central database which can be interrogated to find the location, age, condition and other relevant information about an individual pesticide package.

The objective of PSMS is to prevent pesticides from becoming obsolete by ensuring that they are used before they expire. If products do become obsolete for reasons of age or physico-chemical degradation, then, the systems can also ensure that these products are removed from stocks and dealt with quickly and appropriately. To this end the PSMS and OPMS systems are currently being integrated to provide a complete pesticide life cycle management tool for countries.

Environmental Management Plans

The FAO developed Environmental Management Toolkit (reported on at the 8th HCH and Pesticides Forum) is designed to assist in planning and implementation of projects for the elimination of obsolete pesticide stocks. EMTK guides users through the production of risk assessments (now automated in OPMS), prioritization of action based on comparative risk assessments, selection of central storage sites based on ensuring minimum risk, planning transportation of stocks and preparing for final destruction.

The actions associated with repackaging, cleanup and transportation of obsolete pesticides from their storage location in itself presents many hazards to the workforce involved in the operation, the surrounding population and the environment. It is therefore necessary to produce an environmental management plan that clearly identifies hazards or risks and demonstrates how they will be avoided or mitigated. This is termed an Environmental Management Plan (EMP)

Combining the guidance of EMTK with the data of OPMS goes a long way to generating site specific EMPs. Working methods based on international best practice and regulation for safety in the workplace as well as on extensive field experience can draw upon standard methods and in many cases on Standard Operting Procedures (SOPs) that can be applied to most situations. At present EMPs and SOPs are produced manually on the basis of OPMS data and EMTK guidance. It is hoped that in the not very distant future, EMPs can be generated largely automatically by taking account of available data and drawing on SOPs. Some situations will undoubtedly always need specific solutions, but building on the systems described could accelerate, simplify and standardize working methods in these hazardous situations.

Container Management

Container Management is a problem in almost all developing countries. Wherever pesticides are used, their empty containers are found and they are often used for inappropriate purposes such as drinking water or food storage. The containers have a high market value, but are hazardous. FAO will shortly publish technical guidelines on container management under the *International Code of Conduct for the Distribution and Use of Pesticides.* A key message of these guidelines will be that it is cheap, simple and perfectly possible for all countries to inform and educate pesticide users to triple rinse pesticide containers and place the rinsate into the spray tank for application. In addition users should be taught to puncture pesticide containers in order to make them unusable for other purposes. As a result over 90% of risk from container misuse is eliminated. Systems for collection, recycling, use or disposal of container materials can then be developed in each country.

FAO has also worked with countries affected by desert locust swarms where large volumes of pesticide applications have generated very large number of pesticide containers. Seeking a system that could clean and crush pesticide containers, FAO issues an international tender to which only one company responded. As a result a bespoke system for pesticide drum washing and crushing has been developed and supplied to desert locust affected countries in Western and Northern Africa. The systems developed clean, render unusable and where possible recycle containers As a result of experience modifications have been made to the machine which is about to be supplied to countries in Eastern Africa and the southern Arabian Gulf that are currently dealing with desert locust outbreaks.

ENVIRONMENTALLY SOUND MANAGEMENT OF STOCKS OF OBSOLETE PESTICIDES IN THE RUSSIAN FEDERATION – AN ARCTIC COUNCIL ACTION PLAN (ACAP) PROJECT

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Over the past ten years the Arctic Monitoring and Assessment Program (AMAP) has studied the presence of several pesticides in Arctic biota, water, and air. In 1997, AMAP presented evidence of high levels of a number of pesticides in Arctic animals. In 2002 even more specific information from Russian areas was published, including observations of fresh sources of DDT and toxaphene in the Kara Sea and adjacent areas, suggesting either continued use of DDT and toxaphene or leakage from old stocks. Studies of the cord blood of pregnant women in various indigenous communities in the Arctic showed elevated levels of many of these priority pesticides, indicating transport over long distances.

Russia has one of the largest stocks of obsolete pesticides estimated at more than 24,000 tonnes. This ACAP project was initiated in 2001 to collect information and ensure environmentally sound management of obsolete pesticides stockpiles in 11 priority regions in Northern Russia to remove the threat to the public health and the environment. The project consists of three Phases:

***Phase I** – Development of inventories in selected priority regions of the Russian Federation;*

***Phase II** –Improvement of temporary storage conditions and consolidation of stocks of waste pesticides, identification of unknown stocks as well as assessment and selection of existing technologies and methods for destruction/disposal of stocks.*

***Phase III** – Implementation of a demonstration project for the environmentally sound destruction/disposal of obsolete pesticides.*

Key-words: Obsolete Pesticides, Arctic Council, ACAP, Russia.

Framework for action. Two recent international developments have formed the basis for this initiative: (1) Formation of the Arctic Council, a voluntary organization of like-minded Arctic countries to eliminate pollution in the Arctic, and (2) ratification of the Stockholm Convention, a global treaty to protect human health and the environment from priority persistent organic pollutants (POPs). All eight Arctic nations have signed the Stockholm Convention. POPs are chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of living organisms and are toxic to humans and wildlife. There are currently twelve priority pollutants identified for action under the Stockholm Convention. Ten of these priority pollutants are pesticides. This ACAP Project addresses the management of these pesticides.

2 218 tons of stocks of obsolete pesticides have been discovered so far during the inventory over the eight regions in the Russian Federation (Altai Kray, Arkhangelsk, Magadan, Omsk and Tyumen regions, Republic of Altai, Republic of Komi, Republic of Sakha (Yakutia). In addition to the contributions of the Arctic Council countries, Russian local authorities have contributed substantial funds from their local budgets about 32 mln. rub.

Inventory and safe storage of stocks of obsolete pesticides in the Russian Federation.

Reducing releases of obsolete pesticides from legacy stocks is the objective of several international projects throughout the world. The Arctic Council Action Plan to Eliminate Pollution of the Arctic (ACAP) has been carrying out such a project in the Northern territories of the Russian Federation since 2001. The project was developed as a response to the environmental information presented by the Arctic Monitoring and Assessment Program (AMAP) of the Arctic Council. The major Russian river systems, with the exception of the Volga River, flow to the North, contributing significant amounts of pesticides into the Arctic Basin. This project is carried out under the Arctic Council Action Plan (ACAP) with the participation of the Russian Federation, Canada, Denmark, Finland, the Netherlands, Norway, Sweden, and the USA.

Russia has a large stock of obsolete and prohibited pesticides estimated at more than 24,000 tons. The existing data, prior to this project, indicated the presence of 3000 tons of obsolete pesticides in the northern regions. As the data were based on existing documentation only, it was expected that the comprehensive inventories based on actual warehouse investigations would provide higher results. This was demonstrated by the identification of an additional 1100 tons in eight priority regions. In addition, the existing information contained only agricultural pesticides, and this ACAP Project obtained information on other stockpiles, such as veterinary, forestry, and sanitary pesticides.

At preparatory phase of the Project, ACAP identified 11 Russian priority regions that directly impact the Arctic. These priority regions include Arkhangelsk (including the Nenets Autonomous District), Komi, Krasnoyarsk Krai (including the Taymyr and Evenkiyskiy Autonomous District), Magadan (including the Chukchi Autonomous District), the Republic of Sakha, Tyumen, Kamchatka (including the Koryak Autonomous District), and Murmansk. Sub-arctic regions include Altai Krai (including the Altai Republic), Kurgan and Omsk.

Sources. The reasons for the accumulation of obsolete pesticides in the Northern Russian territories are as follows: pesticides stored too long, i.e., exceeding their shelf-life; changes in product registration and approval, excess quantities provided by off-farm authorities (Soviet legacy pesticides). Leftovers from donations under international development assistance programs. Damage or loss of identity due to poor storage conditions.

Practical lessons.

The implementation of the activities requires the effort of all relevant agricultural, forestry, sanitary and veterinary agencies and experts. It is useful for the project steering committee to meet and work directly with the regional experts to receive the best possible information for the funding decisions and project development. Due to long distances and the large number of warehouses, it is economically desirable to perform all the work (inventory development, assessment of storage facilities, sample collection, repackaging, and transportation to the safe warehouses) in one visit to a district. Weather is a significant constraint in doing this work; therefore advance planning is necessary to ensure completion of all work during the "weather window."

Conclusions. This project is a prime example of actions by the Arctic nations to address the danger of stockpiles of obsolete pesticides in the Arctic. The ultimate objective of the project is the environmentally sound destruction of these obsolete pesticides stockpiles to remove the threat to the public health and the environment. As a result of the successful development and demonstration of this model approach in these Arctic regions, the Russian Federation has agreed to apply this model in other regions of Russia containing stocks of obsolete and prohibited pesticides.

PESTICIDES USE, NATIONAL PROGRAMME AND OBSOLETE PESTICIDES MANAGEMENT IN REPUBLIC OF SLOVENIA

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The Republic of Slovenia (20,273 km2, 2.011,500 inhabitants, 782,533 employees) is one of the smallest European countries. In comparison to the other Central and Eastern European countries, the macroeconomic importance of agriculture in Slovenia is relatively low.

Approximately 55% of Slovenia is covered by forest. In the lowlands, less than 25% is agricultural land. Farming in Slovenia is characterized by its small holdings. The average size of an agricultural holding is about 6.2 ha and only 15% of them are larger than 10 ha. Small scale farming results in lower competition of the Slovenian agriculture in comparison to the European. In Slovenia data on pesticide use is collected for the last 15 years.

This article will present pesticide use by type and quantity in Slovenia in the last 15 years. Pesticide use in agriculture will also be presented on a region-by-region basis; the established quantities of obsolete pesticides will also be shown on this basis. The national programme of activities to remove and/or destroy obsolete pesticides will be outlined, and the activities taking place on the ground to remove these pesticides will be set alongside the current national programme.

An estimate of the amounts of obsolete pesticides that will arise in the next few years will be made on the basis of the quantities and types of pesticides currently being used.

Introduction

Slovenia is one of Europe's smallest countries, covering an area of just 20,250 km2. Its population density – two million people means 99 per square kilometre – is not very high by European standards (only the Nordic countries, Spain, Greece and Austria are less densely settled). An above average proportion of the country is rural: 57.3% of the Slovenian population lives in rural areas, which comprise 89.1% of the entire territory.

Services and industry are the main forms of employment, though agriculture still has a significant role, representing 9.2% of the total employment structure, though that proportion is noticeable on the decrease. The relative importance of commercial sectors means that services (63.6%) play a major role in the national economy. Industry contributes 30.4% to total GDP, agriculture just 3.1%.

The use of plant protection products in the past five years continues to increase, and rose from 1,495 tonnes in 1995 to 1,602 tonnes in 2000. The total usage of such products per hectare of agricultural land was 3.1 kg/ha. Fungicides and bactericides represent over half of the quantity of products used (55%), while herbicides represent 27%, insecticides 12% and other products 6%. Over two-thirds of all products were used on family farms, where the average use was 2.4 kg/ha. Slovenia is one of Europe's largest consumers of plant protection products per hectare of cultivated agricultural land.

Use of plant protection products by type and quantity

Between 1995 and 1999 the use of plant protection products on family farms increased from 968 tonnes to 1417 tonnes.

Table 1 indicates the increased use of all plant protection products from 1990 to 1999 by type (fungicides and bactericides, herbicides, insecticides and other pesticides).

Table 1

Unit	1990	1995	1997	1998	1999
Total (t)	2,212	1,495	1,452	1,526	1,602
Fungicides and bactericides (t)	1,045	693	694	839	886
Herbicides (t)	634	418	478	428	432
Insecticides (t)	417	260	180	154	192
Other pesticides (t)	116	124	100	105	92

Figure 1 illustrates the sale of plant protection products in the Republic of Slovenia from 1992 to 2004 in active constituent kilograms.

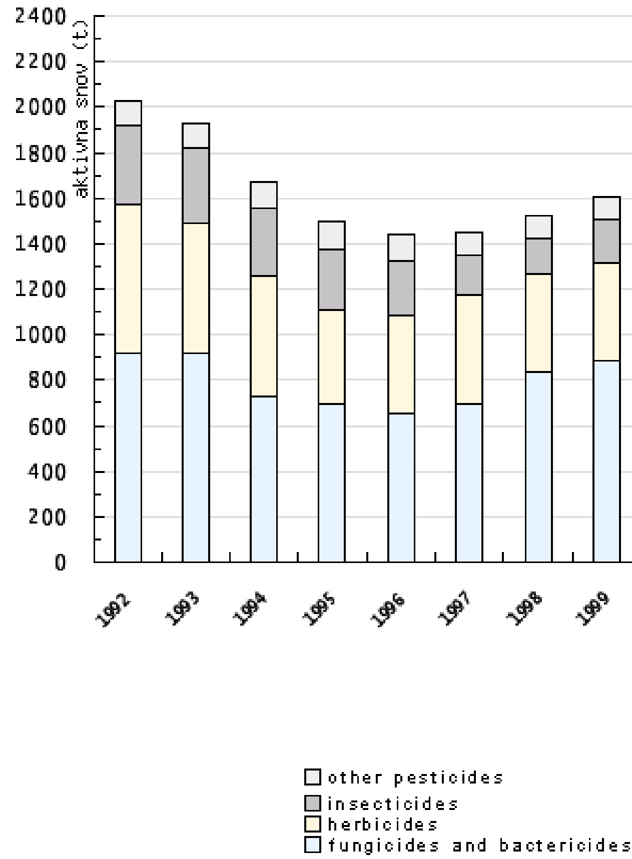


Table 2 indicates the increased use of plant protection products on family farms from 1990 to 1999 by type (fungicides and bactericides, herbicides, insecticides and other pesticides).

Table 2

Unit	1990	1995	1997	1998	1999
Total (t)	481	968	982	1.072	1.147
Fungicides and bactericides (t)	703	426	450	621	636
Herbicides (t)	428	275	336	289	312
Insecticides (t)	259	188	141	118	129
Other pesticides (t)	91	79	55	44	70

Table 3 indicates the increase in total sales of plant protection products on the Slovenian market (active constituent kilograms) from 2000 to 2002 by type (fungicides and bactericides, herbicides, insecticides and other pesticides).

Table 3

Unit	2000	2001	2002
Total	1,464,110	1,398,268	1,471,927
Fungicides	842,594	932,718	936,687
Herbicides	408,532	365,894	384,981
Insecticides	97,966	80,905	109,457
Other pesticides	119,017	18,751	40,802

In 2001, plant protection products registered in the Republic of Slovenia contained 215 active constituents. The method of applying these products is important, as well as the quantity. In 2001 there were nine authorised organisations registered with the Ministry of Agriculture, Forestry and Food to test devices for the use of plant protection products on the ministry's behalf. These organisations performed 3668 inspections (2382 inspections of sprinklers, 1277 inspections of spraying and sprinkling devices, and 9 inspections of motor sprayers and sprinklers), producing 3614 written reports on inspections performed.

The annual consumption of plant protection products on farms totalled 3.4 kg/ha of cultivated land. The highest use is on hilly lands – 9 kg/ha, much less elsewhere: 2 kg/ha on plains, and 1 kg/ha in highlands and Karstic land. Half of all agricultural holders used up to 1 kg/ha of plant protection products. Agricultural holders used 110 different plant protection products, with eight products of particular note by quantity: Sulphurbased preparations, Primextra, Dithane, Dual, Ridomil, Polyram, Antrazine and Radazin. Five are fungicides, and three are herbicides.

Primextra is a dual action grass and broadleaf herbicide. The active constituents are metolachlor and atrazine.

Dual is a herbicide used to protect corn, sunflowers, soya and sugar beets, the active constituent is metolachlor.

Atrazine and Radazin are herbicides with the active constituent atrazine.

There is a difference in pesticide use between the agricultural enterprises and family farms. For example: in 1998 agricultural enterprises used six times more pesticides than family farms.

Table 4 indicates sales on the Slovenian market for 2000 by the active constituent (in kgs) of plant protection products.

Table 4

	Active constituent	Quantity (kg)
1.	Atrazine	39,577,789
2.	Bentazon	12,404,145
3.	Diuron	374,880
4.	Glifosat	70,096,032
5.	Izoproturon	3,623,500
6.	Chlortoluron	38,226,000
7.	MCPA	1,656,670
8.	MCCP (mecoprop)	1,790,050
9.	Mecoprop-P	2,399,400
10.	Simazin	4,199,000
11.	Terbutilazine	7,852,800
12.	Alachlor	3,849540

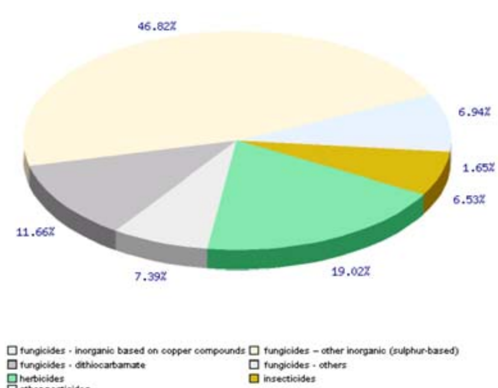


Figure 2: Proportion of sales for plant protection products in the Republic of Slovenia for 2004

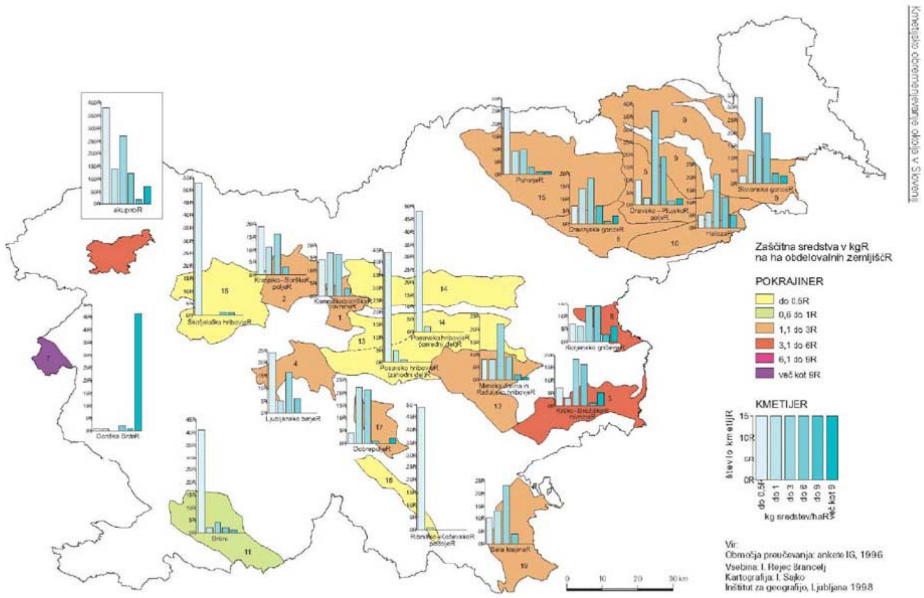


Figure 3 illustrates the use of plant protection products by Slovenian region.

A major problem for farmers on family farms is a lack of information and a lack of knowledge regarding sprinkling on cultivated land. Thirteen per cent of farmers simply act according to their own experiences, 20% of farmers act according to their own experiences and advice from specialists, with approximately half following the instructions from producers and sellers of plant protection products. Only 78% of private farmers answered correctly when asked about the expiry date for plant protection products; 31% of farmers on family farms did not use PPE when sprinkling, 17% used protective clothing, and 17% used just a mask. Approximately one tenth of private farmers disposed of unused plant protection products by pouring it into land or running water.

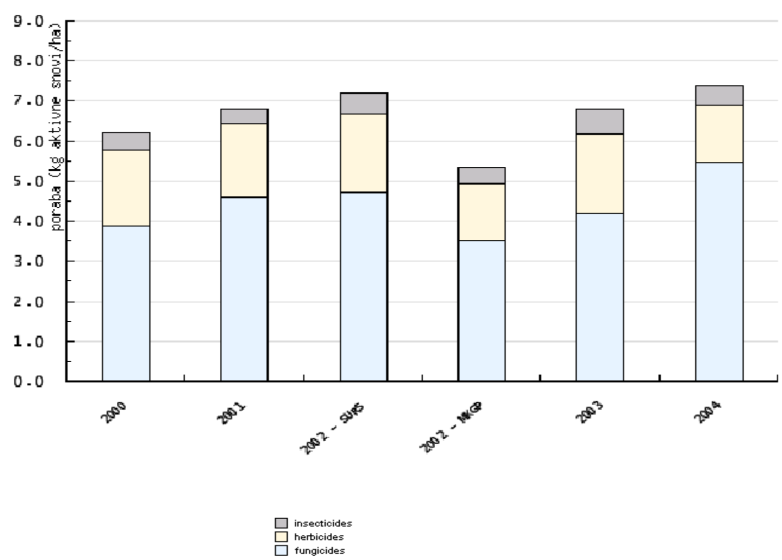


Figure 4 illustrates the consumption of plant protection products per hectare of cultivated land in Slovenia.

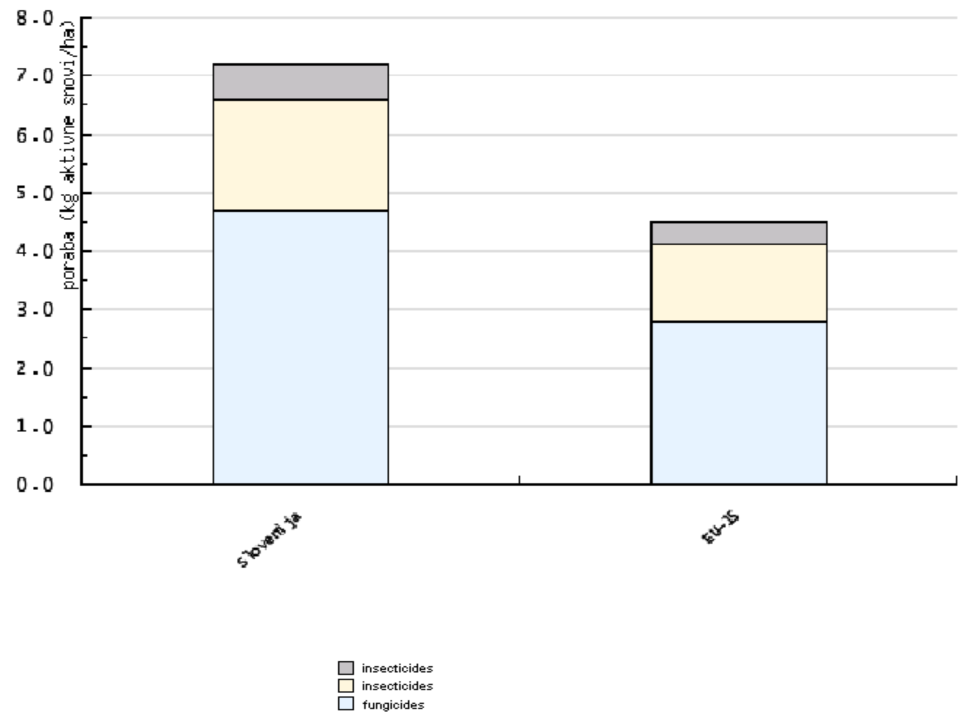


Figure 5 illustrates the consumption of plant protection products per hectare of cultivated agricultural land in the European Union (EU-15) in 1999 and in Slovenia in 2002.

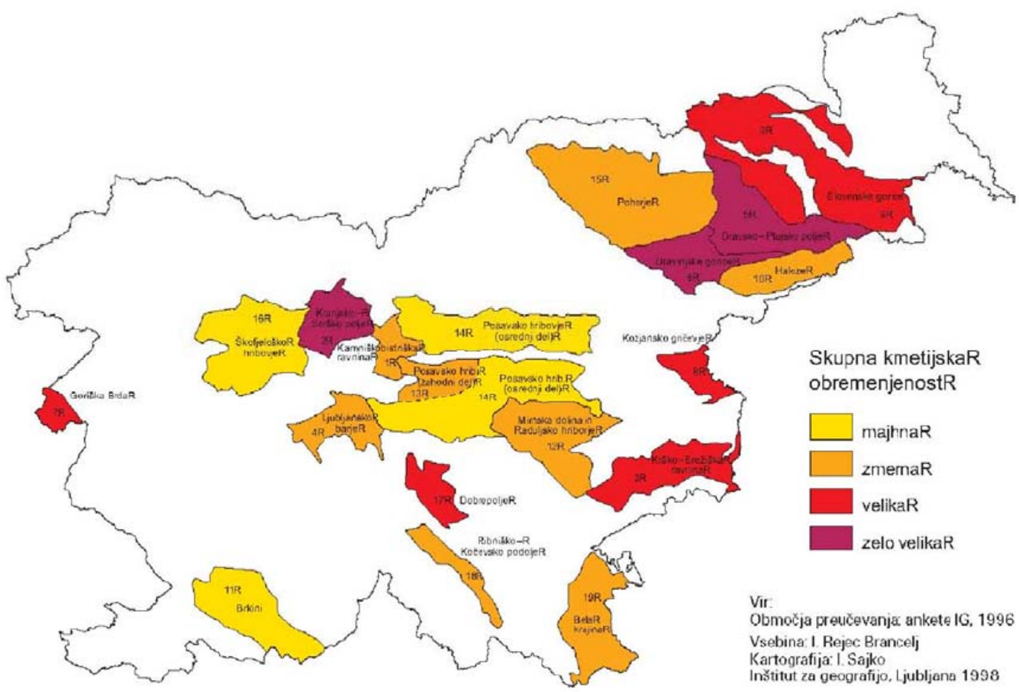


Figure 6 indicates pollution in Slovenia from the use of plant protection products in 1996.

Legislation on plant protection products in the Republic of Slovenia

Ministry of Agriculture, Forestry and Food is the competent body for preparing legislation and for registration, trade and usage of plant protection product in Slovenia.

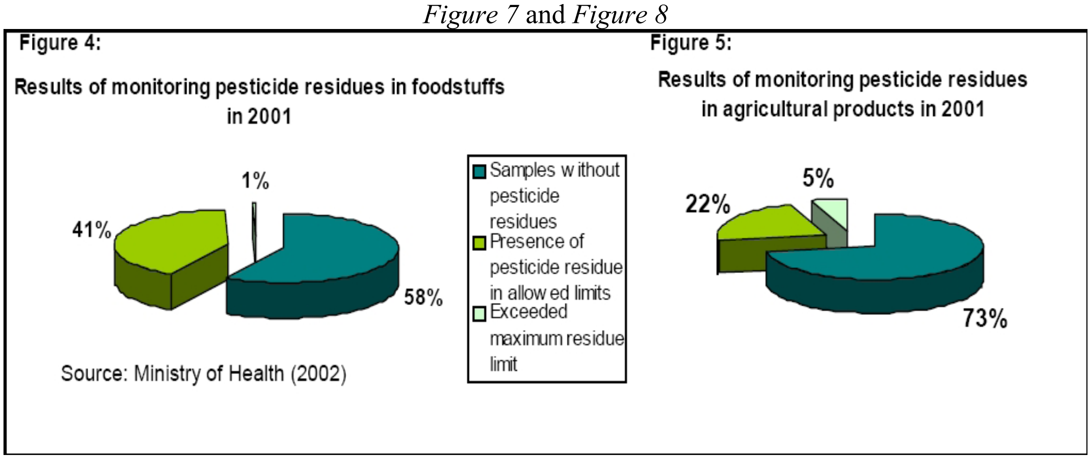
The currently valid legislative acts in the field are:

- Plant Protection Product Act, Official Gazette RS 35/2007,
- Rules on Plant Protection Product Licences, Official Gazette RS 36/2003
- Rules on the Composition and Working Methods of Plant Protection Product Commission, Official Gazette RS 74/2002
- Decree on the Supplementary Protection Certificate for Plant Protection Products, Official Gazette RS 62/2003,
- Rules on Additional Standard Warnings and Notifications for Plant Protection Products, Official Gazette RS 31/2004,
- List of Active Constituents with a Licence for Use as Plant Protection Products in EU Member States and the Republic of Slovenia, Official Gazette RS 94/2001
- Supplemented List of Active Constituents with a Licence for Use as Plant Protection Products in EU Member States and the Republic of Slovenia, Official Gazette RS 34/2003,
- Decree implementing the Regulation of the Council concerning the Creation of a Supplementary Protection Certificate for Plant Protection Products, Official Gazette RS 42/2004
- Decree on Fees relating to the Registration of Plant Protection Products, the Evaluation of Active Constituents, and Issue of Plant Protection Product Licences, Official Gazette RS 36/2005
- Decision prohibiting the Placing on Market and Use of Certain Toxic Substances and Preparations based thereon as Plant Protection Products, Official Gazette RS 29/1996.

These acts link the monitoring and testing of foodstuffs to pesticide content. The following sentence was published in: Pesticide Use in Slovenia (1):

- In 2001 residues of different substances were determined in the official food monitoring. Presence of pesticide residues up to maximum residue limits (MRLs) was determined in 69 samples of foodstuffs (41.1%) and in 33 samples of agriculture products (21.9%). MRLs were exceeded in 1 % of foodstuff (1 sample bread) and in 5% of agricultural products (8 samples, lettuce and potato) – Figure 7 and Figure 8.

Figure 7 and *Figure 8*



The *Programme for the Prevention of Pollution of Water Environment caused by Dangerous Chlorinated Hydrocarbons from Diffuse Pollution Sources*, which is part of the National Environment Protection Programme published in Official Gazette RS 83/99, also has a partial legal basis in the above-stated legislative acts.

The programme to prevent the pollution of water with chlorinated hydrocarbons is based on implementing regulations. These relate to emission limit values for chlorinated hydrocarbon emissions into the air and monitoring data on the quality of surface waters.

Six of the pesticides listed in Table 5 are deemed as chlorinated hydrocarbons in the aquatic environment.

Types of chlorinated hydrocarbons covered by the Program for the Prevention of Water Pollution

Table 5

Chlorinated Hydrocarbon Type	Chemical Formula of Hydrocarbon
Trichloroethane	C2HCl3
Tetrachloroethane	C2Cl4
Trichloromethane	CHCl3
1,2-dichloroethane	CH4Cl2
Tetrachloromethane	CCl4
1,2,4-trichlorobenzene	C6H3Cl3
Hexachlorobenzene	C6Cl6
Hexachlorobutadiene	C4Cl6
Hexachlorocyclohexane (lindane)	C6H6Cl6
Pentachlorophenol	C6HCl5O
Aldrin	C12H8Cl6
Isodrin	C12H8Cl6
Dieldrin	C12H8Cl6O
Endrin	C12H8Cl6O
DDT*	C14H9Cl5

**DDT includes the isomer p,p-DDT, o,p-DDT, p,p-DDE and p,p.-DDD (DDT – 2,2 – bis (p-chlorophenyl) – 1,1,1 – trichloroethane).*

These chlorinated hydrocarbons are classified into three groups:

1. The first group includes chlorinated hydrocarbons subject to European Union decisions concerning the implementation of the Stockholm Convention and the POPs Protocol. The following belong to the first group: aldrin, dieldrin, endrin, hexachlorobenzene, DDT and hexachlorocyclohexane, including lindane.

2. The second group comprises chlorinated hydrocarbons which are present in Slovenia in negligible amounts according to chemical analysis, and which should not have a negative effect on surface waters. The following belong to this group: pentachlorophenol, hexachlorobutadiene, trichlorobenzene, tetrachlor-methane and 1.2-dichloroethane.

3. This group of chlorinated hydrocarbons includes those used in significant quantities according to existing findings. They include: trichloroethane, tetrachloroethane and trichloromethane.

Dangerous chlorinated hydrocarbons are already partially regulated by existing Slovenian environmental protection legislation. Further legislative regulations will be required to regulate the control and handling of hydrocarbons covered by the Programme, and they are already being prepared by the Ministry of the Environment and Spatial Planning.

The substances from the first group include plant protection products, so below only emission and immission values for these substances and only into waste water, as their use in agriculture, i.e. entry into the ground is already prohibited. This also prohibits the import of these substances and their placing on the market for agricultural purposes. They may be used for other purposes, such as impregnating timber, impregnating fibres and textiles, as synthetic or process reactants in industry, to protect construction timber and buildings of cultural and historical importance, etc.

Permitted emission values for the release of chlorinated hydrocarbons into waste water

The permitted values for emission into wastewater are regulated by the Decree on the Emission of Substances in Waste Water Discharge from Plants and Facilities for the Manufacture of Plant Protection Products (Official Gazette RS, 84/99).

Permitted emission values are given in Table 6.

Industrial activity	Emission limit values for concentration of dangerous chlorinatedhydrocarbons (mg/L)		Emission limit value factor (g/t)	
	Average daily concentration value	Average monthly concentration value	Daily emission factor	Monthly emission factor
DRINS				
Production and processing of aldrin and/or dieldrin and/or endrin and/or isodrin in same location	0.01	0.002	15.0	3.0
DDT				
Production and processing of DDT in same location: - existing source - new source	 0.4 0.2	 0.2 0.1	 8.0 1.0	 4.0 0.5
HEXACHLORO BENZENE				
Production and processing	2.0	1.0	20.0	10.0
HEXACHLORO CYCLOHEXANE				
Production	4.0	2.0	4.0	2.0
Extraction of lindane	4.0	2.0	8.0	4.0
Production of HCH with extraction of lindane	4.0	2.0	10.0	5.0

The Decree states that the annual emission value for dangerous substances is defined with respect to a medium-low water flow into which technological water flows from the exact point of pollution.

Permitted emission values for the release of chlorinated hydrocarbons into ground

The Decree on Limit, Alert and Critical Immission Values of Dangerous Substances in oil (Official Gazette RS, No 68/98) states that the limit value for drins is 0.1 mg/kg of dry soil, the alert value 2 mg/kg of dry soil and the critical value 4 mg/kg of dry soil. The limit, alert and critical values apply to the total concentration of aldrin, dieldrin and endrin. The limit value for the total concentration of DDT/DDD/DDE is 0.1 mg/kg of dry soil, the alert value 2 mg/kg of dry soil, and the critical value 4 mg/kg of dry soil. The decree also defined values for hexachlorocyclohexane compounds.

Results of Surface Water Immission Monitoring Programme

The programme for monitoring surface water quality includes measurements of aldrin, dieldrin, endrin and DDT-isomers: p,p-DDT, o,p-DDT, p,p-DDE, o,p-DDE, p,p-DDD and o,p-DDD. Hexachlorobenzene and isomers of hexachlorocyclohexane in surface water is also measured: α-HCH, β-HCH, γ-HCH and δ-HCH. The hexachlorobenzene and hexachlorocyclohexane content is also monitored in sediment up to a depth of 15 cm. The number of sampling points, their geographic distribution and the sampling frequency are adapted each year to the requirements of the specific watercourse. Sampling to detect these dangerous chlorinated hydrocarbons is carried out up to twice a year, and the results of surface water immission monitoring are given in Tables 7 and 8 below.

Data on surface water content of aldrin, dieldrin and endrin and DDTs from 2000 to 2002 (measurements of o,p-DDT and o,p-DDE started in 2001, measurements of isomers of p,p-DDD in 2002)

Table 7

Year monitoring executed	Number of sampling points	Number of samples	Maximum annual average value of dange-rous chlorinated hydrocarbo ns (µg/L)	Number of sampling points above detection limit	Number of sampling points exceeding EU quality standard
ALDRIN					
2000	27	34	0.0015	0	0
2001	28	35	0.0010	0	0
2002	27	32	0.0010	0	0
DIELDRIN					
2000	27	34	0.0016	0	0
2001	28	35	0.0010	0	0
2002	27	32	0.0010	0	0
ENDRIN					
2000	27	34	0.0015	0	0
2001	28	35	0.0015	0	0
2002	27	32	0.0015	0	0
p,p-DDT					
2000	27	34	0.0025	0	0
2001	28	35	0.0020	0	0
2002	27	32	0.0020	0	0
o,p-DDT					
2001	28	35	0.0015	0	0
2002	26	31	0.0015	0	0
p,p-DDE					
2000	27	34	0.0015	0	0
2001	28	35	0.0015	0	0
2002	27	32	0.0015	0	0
o,p-DDE					
2001	28	35	0.0010	0	0
2002	26	31	0.0010	0	0
p,p-DDD					
2002	27	32	0.0015	0	0
o,p-DDD					
2000	27	34	0.0015	0	0
2001	28	35	0.0015	0	0
2002	27	32	0.0015	0	0

Table 8 gives the data for surface water content of hexachlorobenzene and individual isomers from 2000 to 2002. The quantification limit for α–HCH was 0.002 µg/L. The quantification limit was 0.003 µg/L for β-HCH, 0.002 µg/L for γ-HCH and 0.003 µg/L for δ-HCH.

Table 8

Year monitoring executed	Number of sampling points	Number of samples	Maximum annual average value of HCB or HCH (μg/L)
Hexachlorobenzene			
2000	27	34	0,0005
2001	28	35	0,0005
2002	27	32	0,0005
δ -HCH			
2000	26	33	0,001
2001	28	35	0,001
2002	27	32	0,001
β -HCH			
2000	26	33	0,0015
2001	28	35	0,001
2002	27	32	0,001
γ -HCH (lindane)			
2000	27	34	0,001
2001	28	35	0,001
2002	27	32	0,001
δ-HCH			
2001	28	35	0,0015
2002	27	32	0,0015

The results of surface water monitoring indicate that the environmental quality standard was not exceeded at any sampling point.

The results of surface water emission value monitoring from 2000 to 2002 indicate that the environmental quality standard was not exceeded at any sampling point.

Measures to reduce chlorinated hydrocarbon emissions

The Decree on the Emission of Substances in Waste Water Discharged from Plants and Facilities for the Manufacture of Plant Protection Products (Official Gazette RS, 84/99) prohibits the discharge of waste water into watercourses or sewage systems.

The Decree on the Emission of Dangerous Halogenated Hydrocarbons in Waste Water Discharge (Official Gazette RS, no 84/99) sets out the following special measures to reduce the environmental pollution from waste water:

- use of synthetic procedures with a high substance and energy recovery with optimal reaction management and optimal control of machinery and devices
- use of production procedures that enable highest possible recycling rate and reuse of useful raw materials, active substances and excipients
- use of active substances and excipients containing the least dangerous constituents possible and causing the lowest possible disturbance to the waste water cleaning process, or their replacement with less dangerous, biodegradable substances
- re-circulation or re-use of process water, with interim cleaning and separation of less polluting partial waste water flows if required
- use of water-saving procedures in washing and cleaning processes, such as countercurrent cleaning, re-circulation of washing water, and high-pressure cleaning processes
- prioritizing use of non-water processes to clean waste air
- processing mother liquors for repeat material and thermal use of constituents
- use of retention tanks to balance release of waste water, and
- use of other technological processes to reduce environmental pollution from waste water.

The measures to reduce the emission of dangerous chlorinated hydrocarbons into the aquatic environment in future include a prohibition on the use of some plant protection products containing specified active constituents. This is covered by an Order (Official Gazette RS, No 105/01), and relates to plant protection products containing one or more of the following active constituents: aldrin, dieldrin, DDT, endrin, hexachlorobenzene, and 1,2-dichloroethane, and salts thereof. The Order also prohibits the placing on the market or future use of hexachlorocyclohexane and compounds thereof, and quintozene and compounds thereof.

The measures aimed at reducing emissions include the Order on the Handling of zone-Depleting Substances (Official Gazette RS, No. 80/976 and 41/2001). This Order stipulates a complete prohibition on the import and placing on the market of ozone depleting substances, and carbon tetrachloride in particular. Import is permitted in exceptional circumstances only on the basis of a special ministry permit, if the substances are required for urgent medical, research or analysis purposes in laboratories. These forms of import are only permitted for recognized users.

Conclusion

Based on the data set out in this report, the Programme of Pollution of the Aquatic Environment caused by Dangerous Chlorinated Hydrocarbons and other legislation relating to the use of plant protection products in Slovenia significantly reduce the use of such products. This will lead to an increase in the quantities of old pesticides that will have to be destroyed. The following actions will be introduced:

- optimising the monitoring of pesticide residue in foodstuffs;
- reducing pesticide residues to the detectable limit, which means no pesticide residue in food, agricultural products and water;
- monitoring of agricultural producers according to type and mass of pesticides used and ensuring that pesticide users are informed and trained, and continual product monitoring;
- increasing the awareness of the public, consumers, farmers, and politicians about the harmful use of excess quantities of pesticides for the production of agricultural products and warning about potential health threats;
- promoting and supporting the implementation of plans to reduce pesticide use and support for coordinated development of agriculture towards organic food production;
- publishing data on the pesticide content of agricultural products;
- promoting integrated plant protection through financial incentives;
- prohibitions or use of pesticides, pursuant to Directive 79/117/EEC;
- controlling sprinkler techniques;
- detailed definition of water protection regions;
- control of pesticide use on non-agricultural land;
- control of pesticide handling and destruction of old stock.

References:

1. Pesticide Use in Slovenia, Pesticide Action Network Germany in cooperation with Association Agrolink 2004, Principal Author: Organisation ECHo ecology cultural diversity health, Edited: Susanne Smolka.
2. Programme for the Prevention of Pollution of the Aquatic Environment caused by Dangerous Chlorinated Hydrocarbons from Diffuse Pollution Sources, part of the National Environmental Protection Plan, Official Gazette RS 83/99.
3. Environmental indicators in Slovenia, Use of Plant Protection Products, Institute of Agriculture of Slovenia, Ljubljana 2006.
4. Irena Rejec Brancelj, Agricultural Environmental Pollution in Slovenia, Landscape Aspects of Agricultural Pollution from Dispersed Sources, Institute of Geography, Ljubljana 2001.
5. Waste Water Monitoring Programme, Ministry of the Environment and Spatial Planning, Ljubljana 2004.
6. Official Gazettes of the Republic of Slovenia.

PRACTICAL EXPERIENCE IN DEVELOPING POPs INVENTORIES IN UKRAINE

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The report represents the practical experience in developing and realization of a comprehensive methodological approach to collecting and processing the data on different sources of the environment pollution by hazardous chlorine-containing substances, persistent organic pollutants (POPs) in particular. The main principals for elaboration of the relative informational system, including the database on the revealed hot-spots and the sites suspected of having harmful impacts on the environment, are also considered. The practical experience in the usage of this methodological approach was got within the international projects realized under the aegis of the Ministry of Environmental Protection of Ukraine. The opportunities for design and realization of a comprehensive information campaign aimed at decision-makers and potential stakeholders, as well as perspectives for R&D, methodological and organisational support and supervision of the National Programmes and Ukraine's obligations in the framework of the international conventions and agreements related to chemicals and waste management are also analyzed.

Key words: persistent organic pollutants (POPs), polychlorinated biphenyls (PCBs), inventory, database, informational system, data collecting and processing, methodological approach

Introduction

Contamination of the environment by hazardous chemical substances, persistent organic pollutants, in particular, is one of principal factors of unfavourable ecological situation in Ukraine and in the whole world. Abilities of POPs to remain persistent within prolonged time in the environment and to spread over large distances from sources of occurrence cause the necessity to control and manage their handling at the international level. The prognostication of ecological situation and development of measures for their improvement at the national level are possible only on the basis of the approved international system for POPs inventory that is specified in corresponding international documents.

Realization of the Canadian POPs Trust Fund / UNEP Chemicals Project Project "Developing an Inventory of Polychlorinated Biphenyls (PCBs) and the Review of Technical and Economic Requirements for Environmentally Sound Technologies of Treatment /Destruction of PCBs", the DEPA-DANCEE and COWI Projects "Assistance to the Ukrainian Environmental Authorities Management of Contaminated Sites" and "Elimination of Risks Related to Stockpiled Obsolete Pesticides in Ukraine" realized under the aegis of the Ministry of Environmental Protection of Ukraine had to promote solving a number of problems related to the POPs issues within the country in general, as well as for development of the national strategy aimed at the decrease of emissions and elimination of hazardous substances in Ukraine. It was considered that these Projects should be a preliminary stage to the development of a National Plan for implementation of the Stockholm Convention on POPs.

Overall methodological approach

The main objective of the Projects was to support Ukraine's central and local administrations in the management of the sites, where POPs or other toxic contaminants were used, stored or located. This should be achieved through the implementing of inventorying procedures for the establishment of an overview of such sites and to evaluate the amounts of contaminants and give priority to the sites according to their potential for harmful impact on the environment and human health. Such inventorying and ranking was used in order to target the most urgent problems and take adequate action and to stimulate programmes for the rehabilitation of most dangerous sites and for the prevention of future contamination of soil and groundwater.

In pursue of the indicated objective the following components and outputs were defined and carried out:

- Identification and inventorying of PCBs sources, as well as the sites contaminated and potentially contaminated with different hazardous substances; ranking according to environmental risks
- Preparation of the methodology, including the ranking system
- Preparation of databases
- Training of the local administrations personal in inventorying procedures

These main components included:

- analysis of the production and types and PCBs usage, as well as technical specifications for the electrical equipment containing PCBs;
- elaboration of the corresponding guidance – separately, on revealing and identification of polychlorinated biphenyls in products and waste, and the sites contaminated and potentially contaminated with different hazardous substances (within different projects);
- making a format of reports for and instructions on how to fill them;
- development of the software for processing the obtained data using computer technologies;
- approval and adoption of elaborated documents in due order;
- appointing persons responsible for the inventory in regions of Ukraine, formation of regional work teams;
- delivery of the reporting forms to enterprises, central and local administrations;
- collection of the filled forms by territorial administrations of the Ministry of Environmental Protection (MEP);
- generalization of the information, submission it to the National Center for Hazardous Waste Management of the MEP;
- processing of the data, analysis of the results, in particular:
  - ▪ processing of the data, developing the database on the types of the equipment and materials containing PCBs including also the information on their quantity and location;
  - ▪ analysis of the obtained information related to types of application and storage of PCBs at enterprises in Ukraine depending on the territory and branch (type of activity);
  - ▪ developing the database on the sites contaminated and potentially contaminated with different hazardous substances, including POPs.

The principal component of the projects comprised the inventorying of POPs sources, contaminated and potentially contaminated sites in Ukraine. The first step in the process of the development of a strategy for management of contaminated sites is the establishment of an overview of the character and extent of the problem. This was accomplished by establishing an inventory of PCBs sources, as well as contaminated sites and sites that possibly might affect negatively by former or ongoing industrial and waste disposal activities. The inventory system was unified and covered all Ukraine.

Focus was put on the point sources as the most harmful effects normally were related to these sources. Diffuse contamination can be found in all industrial and urban areas in concentrations that can be harmful under more extreme circumstances and therefore, this aspect might be considered in future projects. The inventory therefore only included point sources. At this stage of the process it was not possible to provide specific data on the degree of contamination on each site. The types of data included in the inventories comprise information on the activities, localisation and basic information on environmental interests.

The main challenge in the inventorying process was to identify the relevant sites, whereof it was expected that many for some reason were not registered within the regulatory system, e.g. closed down industries, illegal activities and military sites. The ambition of the first effort for identifying contaminated sites was to identify sites contaminated with toxic substances, including POPs, and sites where toxic substances were handled and therefore posed a risk for human exposure (directly or indirectly). A specified list of objects for the registration of sites was elaborated and enclosed to the guidelines prepared for the data collection work.

Database system

A database system for the inventorying of the contaminated sites was designed and prepared within the framework of the existing "Chestnut" system developed for environmental management of information related to facilities of generation, processing, recycling and disposal of waste. The system is used to register and provide information on waste generation, quantitative and qualitative composition, handling and reduction as well as exercising of control of impact on natural environment and public health.

The Chestnut system applies to valid legislative acts of Ukraine, is based on state codes and classifiers and relates to procedures approved by corresponding Resolutions of the Cabinet of Ministers of Ukraine. The system including relevant classifiers and registered industries within each region has been distributed to and implemented by the environmental departments in all Ukrainian regions. By that, it was established an electronic link between these departments and the National Center for Hazardous Waste Management. Procedures for regions' reporting with the usage of that link were established and validation procedures were implemented within data processing.

Conclusions and recommendations

As a result of the work conducted, the database on the availability of the equipment and synthetic fluids, containing PCBs, was created, including the data on their type, quantity and location. It is the overall conclusion that the mentioned projects implementation and the corresponding results met the defined objectives. However, the inventorying and related activities aimed at the development of a strategy for a national approach to the problems arising from POPs contaminated sites need continuation under further administration support and to be given priority by the Ministry of Environmental Protection of Ukraine.

This conclusion is strongly supported by the feedback from the local administrations in the questionnaire survey carried out for recollection of the ideas from regions and recommendations to future actions. One of such requested actions is development of the inventorying activities with GIS-facility.

OBSOLETE PESTICIDES MANAGEMENT - ECONOMIC COST MODEL FOR OBSOLETE PESTICIDES HANDLING

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An economic model was developed to be used for the planning of obsolete pesticides inventories, repacking, collection, transporting, storage and final destruction. The cost model was developed in connection with a project on environmentally sound management of Obsolete Pesticides (OPs) in two regions in the Russian Federation: Pskov and Vologda. The project was funded by the Danish Ministry of Environment. The project provided assistance in the two oblasts to prepare inventories of OPs; develop plans for future management and disposal of OPs; and demonstrate safe and environmentally sound management of obsolete pesticide stockpiles.

The aim of the cost model was to provide useful input to the decision makers, namely the oblast authorities, in the process of developing an action plan for an environmentally sound management of OPs. The model computes the direct cost associated with disposing the OPs in an oblast based on OPs quantity data, location, distance, storage facilities, central storage facility etc. The model computes the various cost elements for the entire elimination process from OPs identification to their ultimate disposal.

The cost model can be used at an initial phase of the development phase before the inventory of the OPs stocks and at a later stage of the development phase after the inventory. In the early state the cost estimate will not be very precise as the quantities of OPs stocks as well as their location will be rough estimates. Later in the process, when the inventory has been prepared, the model will yield more accurate cost estimates based on more accurate data on quantities, locations, distances, storage facilities, etc.

The model is Excel-based with a user-friendly interface. The target groups of the model are government officers at Plant Protection Stations in charge of designing an action plan for an environmentally sound management of OPs.

Key words: obsolete pesticides, economic model, Russian Federation, action plan.

Background and objectives

Financed by the Danish Ministry of the Environment COWI has carried out 3 major obsolete pesticides projects during the last 5-10 years in Eastern Europe.

The present cost model was developed in connection with a Danish funded project on environmentally sound management of Obsolete Pesticides (OPs) in two regions in Russia: Pskov and Vologda. The project provides assistance to the two oblasts in preparing inventories of OPs; develop plans for future management and disposal of OPs; and demonstrate safe and environmentally sound management of obsolete pesticide stockpiles. The model was developed on the basis of the experiences gathered from the development of the action plan and its implementation in the Oblasts of Pskov and Vologda. The project in ongoing as it has been decided within the Danish-Russian bilateral programme to collect further pesticides.

The aim of the cost model was to provide useful input to the decision makers, namely the oblast authorities, in the process of developing an action plan for an environmentally sound management of OPs.

The model does not attempt to make cost-benefit analysis of OPs management actions plans. This is a highly complicated type of analysis and data requirements are big in order to quantify the benefits in monetary values. In this model the benefits of an environmentally sound management of OPs are assumed to be given. The model is an Excel based cost model enabling to estimate the costs of an environmentally sound management of OPs.

The target groups of the model are government officers at Plan Protection Stations in charge of designing an action plan for an environmentally sound management of OPs.

Model specifications

The cost model gives an overview of the costs of an action plan for an environmentally sound management of obsolete pesticides by calculating the entire costs of an environmentally sound management of OPs. The model covers the entire period from the initial inventory until the OPs are ultimately being destructed.

Based on Oblast specific inputs (such as OPs stocks, quantities, location, storage facilities, etc.), the cost model estimates the cost of each of the main components of the various phases of the action plan:

- Development phase

[1] Inventory (C.1)

[2] Public information activities (C.2)

[3] Identification (C.3)

- Implementation

[4] Repackaging (C.4)

[5] Transportation (C.5)

[6] Storage (C.6)

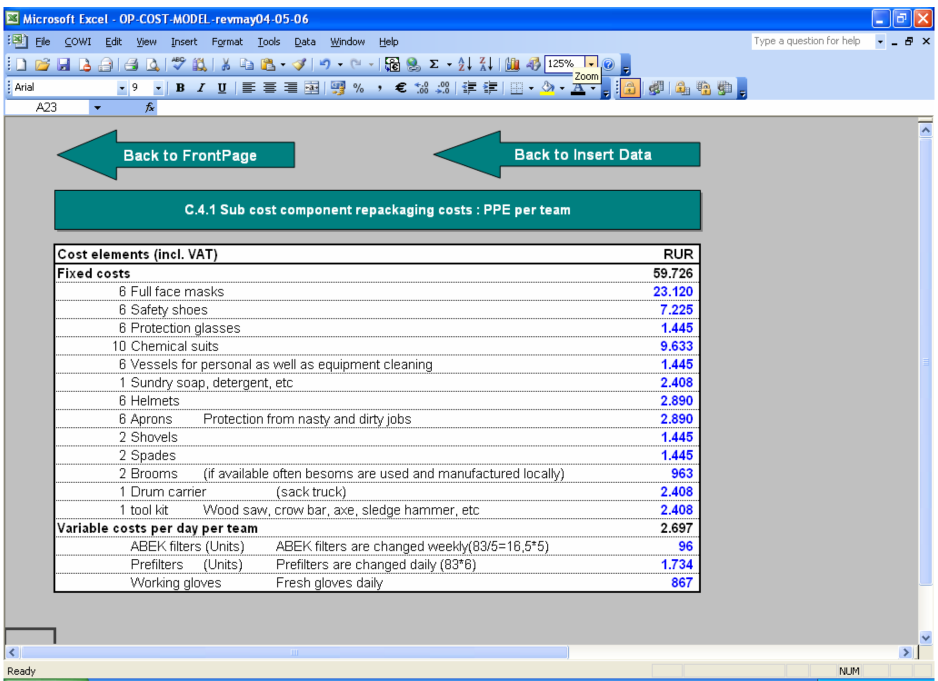
[7] Testing for contaminated sites (C.7)

- Long term strategy:

[8] Elimination (C.8)

The model is based on a user friendly EXCEL spreadsheet with a number of input and output sheets and navigation keys. An example the input sheet for personal protective equipment per team is shown below.

Figure 1: Example of screen dump of input sheet for personal protective equipment



Cost elements (incl. VAT)		RUR
Fixed costs		59.726
6 Full face masks		23.120
6 Safety shoes		7.225
6 Protection glasses		1.445
10 Chemical suits		9.633
6 Vessels for personal as well as equipment cleaning		1.445
1 Sundry soap, detergent, etc		2.408
6 Helmets		2.890
6 Aprons	Protection from nasty and dirty jobs	2.890
2 Shovels		1.445
2 Spades		1.445
2 Brooms	(if available often besoms are used and manufactured locally)	963
1 Drum carrier	(sack truck)	2.408
1 tool kit	Wood saw, crow bar, axe, sledge hammer, etc	2.408
Variable costs per day per team		2.697
ABEK filters (Units)	ABEK filters are changed weekly(83/5=16,5*5)	96
Prefilters (Units)	Prefilters are changed daily (83*6)	1.734
Working gloves	Fresh gloves daily	867

For each cost element, unit prices of the year 2004 were estimated. All costs were calculated in financial costs - as opposed to economic costs. Financial costs are the actual costs (outlays) encountered by the oblast authorities in implementing an action plan. Financial analysis is based on the actual prices that the project entity pays for inputs and receives for outputs. Opposed to financial cost, economic costs express the opportunity cost to society associated with the considered project. The economic costs do not include tariffs, export taxes and subsidies, excise and sales taxes, production subsidies, and others distortions, etc.

The model also provides a cost-effectiveness analysis of the actions plan, and presents the relationship between project costs and outcomes as costs per unit of outcome achieved (e.g. costs per tonne OPs removed).

Results for the oblast of Pskov and Vologda

The main cost driver for the action plan is the quantities of OPs and the assumptions regarding the quantities have a major impact on the total costs. By use of the model, the cost estimates can be easily adjusted as more accurate estimates of the OPs stocks become available. Table 1 shows the model assumptions on the quantities of OPs in the two oblasts.

Assumptions on the quantity data in Vologda and Pskov

Table 1

	Vologda	Pskov
Quantity of obsolete pesticides in stocks in tonnes	216	572
Number of sites with OPs stocks	146	254
Quantity of OPs, tonne per drum	0,06	0,06
Share of unknown pesticides	50%	70%
Share of OPs that need repacking	100%	100%

Estimated costs of action plans in Vologda and Pskov

Table 2

Cost components and sub components		Costs in RUR	
		Vologda	**Pskov**
C.1	**Preparation and conducting the inventory**	**369,406**	**541,114**
	Manpower cost	*183,106*	*322,014*
	Accommodation (lump sum)	-	-
	Equipment	*51,100*	*51,100*
	Transportation costs	*135,200*	*168,000*
C.2	**Public information activities**	**4,600**	**12,400**
	Cost of public information (lump sum)	*4,600*	*12,400*
C.3	**Identification**	**-**	**-**
	Identification cost	-	-
C.4	**Repackaging**	**2,196,031**	**5,689,506**
	Costs of Drums	*1,080,000*	*2,859,900*
	Manpower costs	*470,880*	*1,246,960*
	Accommodation costs	*238,049*	*630,390*
	Transportation of repackaging team	*96,330*	*168,000*
	PPE costs	*59,726*	*119,452*
	Variable PPE costs	*233,045*	*617,139*
	Label costs	*18,000*	*47,665*
C.5	**Transportation**	**804,985**	**1,453,583**
	Transportation costs	*804,985*	*1,453,583*
C.6	**Storage costs**	**4,369,293**	**4,559,213**
	Pallets	*115,200*	*305,120*
	Storage costs	*4,254,093*	*4,254,093*
C.7	**Contaminated sites**	-	-
	Cost of testing for contaminated sites	-	-
C.8	**Elimination**	-	-
	Transportation costs	-	-
	Elimination costs	-	-
Total costs		**7,744,314**	**12,255,815**
	Quantity of obsolete pesticides in stocks (in tonnes)	***216***	***572***
	Number of sites with OPs stocks	146	254
	Cost effectiveness (cost per tonne)	***35,853***	***21,426***

The results of applying the model in the cases of Pskov and Vologda oblasts is shown in table 2. The estimated costs per tonne of OPs, by use of the applied input parameters, ranged from 21.426 to 35.853 RUR/tonne exclusive of the costs of elimination and remediation of contaminated sites. The costs of final elimination of the OPs was not calculated, but using cost estimates of the reports prepared by UNEP Chemicals on destruction of POPs indicate that the total costs of transport and final elimination may quite well be in the order of 35,000-45,000 RUR.

Obtaining the model

The model spreadsheet and the user manual can be obtained for free by contact to Jørn Lauridsen (jql@cowi.dk) or Mikala Klint (mkl@mst.dk).

Acknowledgements

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EFFORTS TAKEN BY BELARUS TO PROTECT PEOPLE AND THE ENVIRONMENT AGAINST OBSOLETE PESTICIDES

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The problem of neutralization and destruction of obsolete pesticides is of a special concern in the sphere of handling dangerous waste.

Totally, over 7,800 tons of obsolete pesticides have been accumulated in the country. Out of this quantity, over 4,000 tons were disposed of in the 70-80s of the 20th century.

Belarus has been taking extensive actions aimed at safely storing of obsolete pesticides. For example, in the recent years, a great bulk of pesticides has been repacked in specialized euro containers, and this work is to be completed in the near future.

Adoption of the National Implementation Plan (NIP) under the Stockholm Convention on Persistent Organic Pollutants (POPs) has become a significant progress in stabilization of the process of handling obsolete pesticides in Belarus.

The problem of complete destruction of obsolete pesticides remains open for Belarus, and it is associated with the risk of migration of pesticides into the environment from burial sites.

In this connection, Belarus, being an economy in transition, is unlikely to independently solve a range of problems related to logistical and engineering support of these tasks without financial assistance and experience of foreign countries.

Key words: pesticides, repacking, burial, destruction, waste.

Currently, over 7,800 tons of obsolete pesticides are accumulated in the country. Out of this quantity, over 4,000 tons were disposed of in the 70-80s of the 20th century in seven burial sites located throughout Belarus.

The main reasons leading to accumulation of pesticides include as follows: ban on the use of already purchased substances due to high toxicity or environmental hazard; low storage stability and high fire hazard; expired periods of use; time-induced reduced mechanical strength and airtightness of the package leading to loss of substances, formation of mixtures and higher fire and environmental hazard at the warehouses. Due to the above, extensive actions have been taken in Belarus to provide safe storage of obsolete pesticides.

For example, in the recent years, pest-killers have been repacked in specialized containers meeting the requirements of the European Agreement Concerning the International Carriage of Dangerous Goods by Road. Totally, over 3 thousand tons were repacked in special 120 l-capacity barrels. Repacked pesticides, including pesticide mixtures, are placed in custodian storage with preliminary sampling for the subsequent identification of a chemical composition.

Of special concern is the condition of pesticides at the burial sites associated with the risk of migration of pesticides into the environment. Each of the burial sites contains organochloride, organopshosphorous, simazine and triazine pesticides and also inorganic compounds and organic acid derivatives.

Currently, after the lapse of 20 years and more from burial of pesticides, the total bulk of the disposed pesticide should be considered as “mixtures potentially related to POPs”. Unquestionably, such a large amount of POPs and POPs-related pesticides at the burial sites requires a continuous monitoring of their environmental impact. This specifically relates to the burial sites which lack the documentation containing the data on constructed protective structures aimed at containment of pesticides in case of precipitation and possibility of ground-water inundation. These two factors define the nature (intensity) of dissolution and migration of pesticides to the underground hydrosphere and subsequent ingestion of pesticides by humans.

Since 2003, RUE Belarusian Research Center "Ecology" has been conducting thorough environmental survey of the pesticides burial sites involving specialized institutions for doing specific types of research. A research performed has resulted in topographic plans of the burial sites, reports on their geological and hydrological conditions, substantiation and construction of monitoring network of observation wells, identification of possible ways of pesticide migration to the environment, comprehensive ecological assessment of burial sites’ impact on natural ecosystems and proposals regarding environmental actions to protect the human health and the environment.

The results of soil survey (soils could be contaminated only during the construction when pest-killers were improperly handled) in the areas of the pesticide burial sites indicate that pesticides are present in the soil in a varying degree. It should be noted that POPs-related pesticides pose a serious hazard to the environment. For example, out of 163 soil samples, 44 samples (27%) were found to contain DDT, 21 samples (13%) – endrin, 6 samples (4%) – dieldrin, 11 samples (7%) – chlordane, 8 samples (5%) – aldrin, and 12 samples (6%) – heptachlor. Therefore, the surveys have revealed that soils contain residual quantities of 6 pesticides being POPs.

It has been found that pest-killers migrate to underground and surface water at all thoroughly surveyed burial sites.

Pesticides are present in underground water in small quantities and their concentration varies within the range of $5x10^{-6}$-$59.8x10^{-6}$ mg/dm^3. They mainly include gamma-hexachlorocyclohexane isomers (GHCH) (including most toxic γ- GHCH) and less frequently – heptachlor and endrin. The maximum permissible concentration is from 0.02-0.004 mg/dm^3.

The continuous monitoring shows that environmental actions should be aimed at eliminating the causes of the pesticides/disintegration products migration from warehouses and remediation of contaminated areas (soil, underground hydrosphere).

To protect the health of the communities residing within the areas of burial sites' impact and also using contaminated underground water as drinking water, it is recommended to impose a tight sanitary control over the quality of water from household water supply sources (pit wells and water wells).

Adoption of the National Implementation Plan (NIP) under the Stockholm Convention on Persistent Organic Pollutants (POPs) has become a significant progress in stabilization of the process of handling obsolete pesticides in Belarus. Basic guidelines of the NIP concerning pesticides are as follows: developing a regulatory and legal framework; remediating contaminated territories; improving awareness of the Belarusian community; eliminating burial sites and neutralizing pesticides and permanently monitoring the environment and health of the people being exposed to pesticides.

Assessing the current situation, it may be stated that complete destruction of obsolete pesticides both in the warehouses and at burial sites is a radical approach of the program under implementation. This target, however, is extremely difficult to address in technological terms and it is also very costly. Being an economy in transition, Belarus lacking experience in the sphere of destruction of such hazardous waste is not capable of addressing this problem alone without financial and engineering support.

THE COMPLEX APPROACH IN SOLVING ENVIRONMENTAL PROBLEMS IN USAGE OF PESTICIDES IN MOLDOVA

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This article refers to the analyses of pesticides used in the Republic of Moldova during a long period of time. It shows that the volume of pesticides used in 1970s-1980s were 30000-40000 tons of the product, but in the last years - 2500-3200 tones or 0,6-0,8 kg/he of active substances. Essentially was changed the assortment of pesticides in Moldova especially those with low resistance, toxicity and danger for people and the environment. The pesticides which were widely used in 1960s-1970s from organochlorine group (DDT, HCH, Heptachlore), the carbomates derivatives (Sevin), mercurum containing compounds for seed treatment, organophosphoates (Chlorophos, Metaphos), 1,3,5 – triazine (Atrazine, Simazine) practically were not used by the end of 80s and beginning of 90s. New products appeared on Moldavian market as: fungicides - inhibitors of stearines and strobulines. Insecticides – new generation of synthetically pyretroides, inhibitors of chitin growth, neopycotinoides. Herbicides – new products from different groups. From all amount of products 92% are referred to III-IV class of toxicity.

In this article also shows the dynamics of restrictions for 54 "old" pesticides including resistant organochlorines in Moldova and in other countries.

In spite of existence of the certain disagreements between the scientists and the public representatives, the chemical plant protection means were applied, and will be applied in the near future. The experience of agricultural production evidently testifies to it, especially in the developed countries. About scales of using the pesticides we can judge. The tendency is those: since 1945 year there was an increase of sales from 0, 2 billions of dollars to 27, 8 billions of dollars, achieved a maximum in 1988-1999 years – 31-32 billions of dollars. After saturation of the world market by pesticides and in connection with the new environmental concept of plants protection, there has come a period of decrease of their sales up to 25,8 billions of dollars. The volumes of application in physical weight were stabilized at a level of 2.3-2.4 billion dollar. The greatest percent comes to herbicides, and then follow insecticides and fungicides.

23-24 % from the global market of pesticides falls to the share of USA.

The wide application of pesticides is connected to their high efficiency. So, in Germany from 1955 till 1988 years the productivity of wheat has grown from 25 centner/ha to 64 centner/ha. The increase is 39 centner /ha, from which 10 centner/ha (25%) comes to improvement of seed-growing and processing of soil, 7 centner/ha (18%) – on application of mineral fertilizers, 7 centner /ha (18%) – on application of retardates and 15 centner/ha (38,4%) – on application of insecticides and fungicides.

Last years the volumes of application of pesticides in the Republic of Moldova reached 1100-1300 tons of active ingredients, that correspond to 0,65-0,75 kg/ha of active ingredients. The countries from EU before its extension used 2,3-2,5 kg/ha active ingredients, and the new joined countries – 0,7-1 kg/ha of active ingredients. Dynamics of pesticides use in Republic of Moldova for last two decades shown in the Fig.1, testifies that since the end of 80s there have been a decrease in volumes of their application from 29000 tones to 2500-3000 tones in 2004-2006. Simultaneously areas processed with pesticides have been reduced with 4,5 million ha (in recalculation to unitary processing) up to 1 million of ha. Analogically to the above example it is possible to note, that yield of agricultural crops closely correlates with protection from harmful organism and with volumes of application of pesticides. For example, by respect of technology and especially protection of vineyards the yield of grapes constituted 60-65 centner /ha in 80s years and more than 30-35 centner /ha in 90's.

In Moldova, as well as in other countries, since 70's of the last century, they began to realize even more, that to widely use the pesticides, it is very important to have them scientifically-proved based on 15-20 criteria, mainly related to the safety for the people and the environment. Otherwise economic, ecological and social losses from use of dangerous pesticides and methods of their application can essentially reduce their benefit. Therefore the pesticides assortment improvement, first of in order to decrease their toxicity and persistence, was given and is given important state importance.

The application of pesticides depending on their destination and chemical structure, which defines the toxicity and persistence, looks as follows:

In 60's beginning of 70's were applied:

– **from insecticides** – persistent organochlorines (DDT, HCH, polichlorcamphen, polichlorpinen, heptachlor), nicotine-containing (anabazdin sulfate, nicotine sulfate), organophosphates (chlorophos, metaphos, carbophos, phosphamid etc.), carbamates (sevin);

– **from fungicides** – copper-fungicide (copper sulfate, copper oxychloride), sulfur-fungicide (grinding, colloidal, moistened powder), dithiocarbamates (policarbazin, polymorzin, zineb, cuprozan), treatment mercury-fungicide for seed;

– **from herbicides 1,3,5 -** triazines (atrazine, simazine, propazine), derivatives of chlorphenoxiacetic acid (salt 2,4-D), derivatives of urea (linuron). High norms of the charge (5-20 kg / ha) copper-containing, sulfur-containing, HCH and some other, gave a large total amount of use of pesticides.

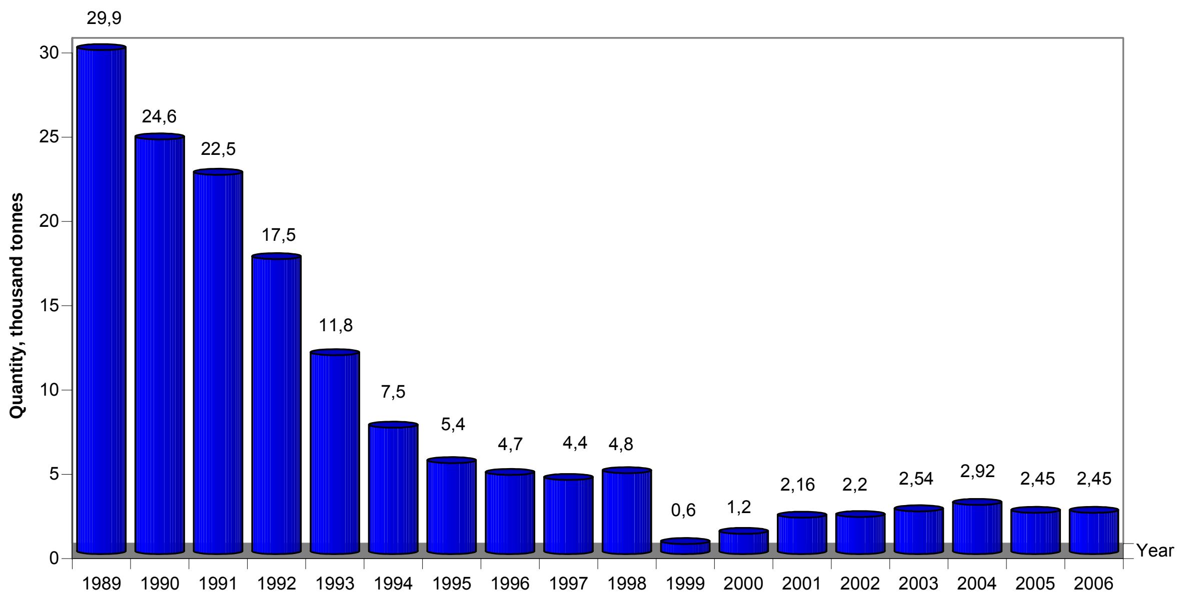


Fig.1 The dinamique of use of pesticides 1989-2006 in Moldova

In 80's from insecticides were widely used organophosphates, appeared synthetic pyrethroids, biopreparations, but were reduced organochlorines. From fungicides were still widely applied copper-fungicide, sulfur-fungicide, but the application of dithiocarbamates was reduced; completely was forbidden application of mercury-fungicide.

The volumes of application 1,2,3 - triazines have decreased simultaneously with occurrence of new generation herbicides.

In 90's on the market were introduced and widely applied:

– **from insecticides** – synthetic pyrethroide, chitin synthesis inhibitors, partially organophosphates;

– **from fungicides** – sterin inhibitors and other groups, but the volumes of application of copper-fungicide and sulfur-fungicide were kept;

– **from herbicides** – new products from different groups. Use of triazines was sharply reduced. This time, common for pesticides was small norms for applying the products.

Such change in pesticide groups promoted improvement of hygienic parameters. For example, the hygienic characteristic of assortment of insecticides and acaricides, submitted in the table testifies that in 60's a share of III and IV group of toxicity made 19 %, and in 2004 – 70,6 %, for the average on pesticides – 93 % and class of danger – 3,2 (tab. 1 and 2).

One of the important criteria for preparations selection and estimation according to sanitary, ecological and toxicological safety is toxic loading. It is expressed by quantity of semilethal dozes for warm-blooded animal, brought in 1 ha of the area during a single processing by pesticides. The preparation having smaller parameter is more ecological. The analysis, carried out by us, shows, that toxicological loading of pesticides, included in the "Register" and used in the republic was essentially changed by decreasing.

So, in 70's the organophosphate products (Bi-58, Zolone, Dursban, Metaphos etc.) were widely applied on apple. Toxicological loading was 2170-11600 mg of active ingredients/ha. In 80's have appeared synthetic pyrethroides (Arrivo, Decis, Fastac etc.). Toxicological loading was one order lower and varied from 200 up to 600 mg of active ingredients/ha at their application. In 90's and in last years with receipt on the market of neonicotinoids (Confidor, Actara, Mospilan, Calypso) both regulators of growth and development of insects, this parameter has decreased for one order and makes 10-150 mg of active ingredients/ha. Analogical situation was also with the fungicides. Copper-containing preparations (copper sulfate, oxichloride of copper) have toxicological loading equal to 4900-11500 mg of active ingredients/ha, dithiocarbamates (Polyram, Dithane M-45, Pencozeb etc.) = 200-300 mg of active ingredients/ha, azol (Score, Topas, Punch etc.), and also strobilurine (Stroby, Flint, Ringo etc.) - (20-80) mg of active ingredients/ha. And nevertheless, despite of occurrence of new groups of preparations having low toxicological loading in the "Register" are included and are applied in the system of protection for the known reasons, though and not so wide as before, organophosphate, Bordeaux mixture and some other pesticides.

According to the analysis of the literature, we make the tables reflecting toxicology of pesticides for bees and entomophage. Therefore at selection of pesticides we pay attention to producers for use first of all of preparations with small and moderate toxicology for shown objects.

Thus, in Moldova at all levels are put the best efforts to maintain the country effective and rather safe pesticides. Unfortunately, there is another problem. It is old come in unsuitability pesticides.

The hygienic characteristic of insecticides used in Moldova

Table 1

Year	Nr.of products	Class of dangerous								Average class of dangerous
		1		2		3		4		
		Nr.	%	Nr.	%	Nr.	%	Nr.	%	
1960	26	15	58	6	23	3	11	2	8	1,69
1970	45	15	33	18	40	10	22	2	5	1,98
1980	71	7	10	23	32	27	38	14	20	2,69
2004	85	0	0	25	29	51	60	9	10,6	2,79

The hygienic characteristic of insecticides used in Moldova

Table 2

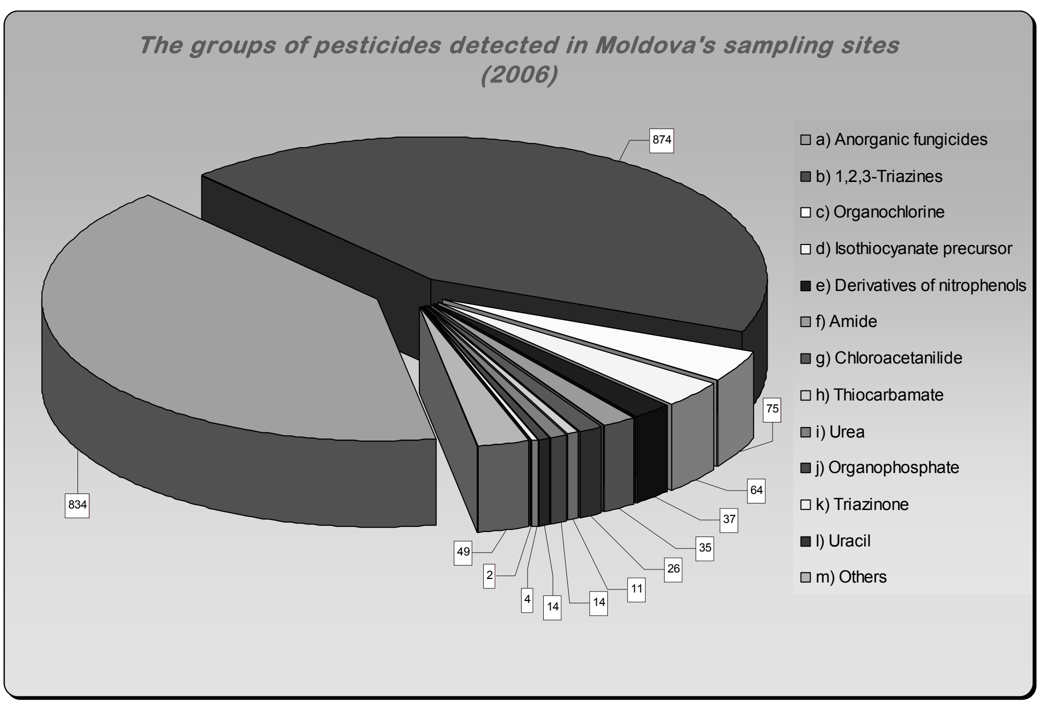
Pesticides	Total	Class of dangerous								Average class of dange-rous
		1		2		3		4		
		Nr.	%	Nr.	%	Nr.	%	Nr.	%	
Insecticides	85	0	0	25	29,4	51	60	9	10,6	2,79
Fungicides	102	0	0	0	0	59	57,8	43	42,2	3,4
Herbicides	105	0	0	0	0	77	73,3	28	26,7	3,27
Seed treatment products	51	2	3,9	2	3,9	37	72,5	10	20,3	3,08
Average (pesticides)	343	2	0,06	27	8	224	65,5	90	26,5	3,17

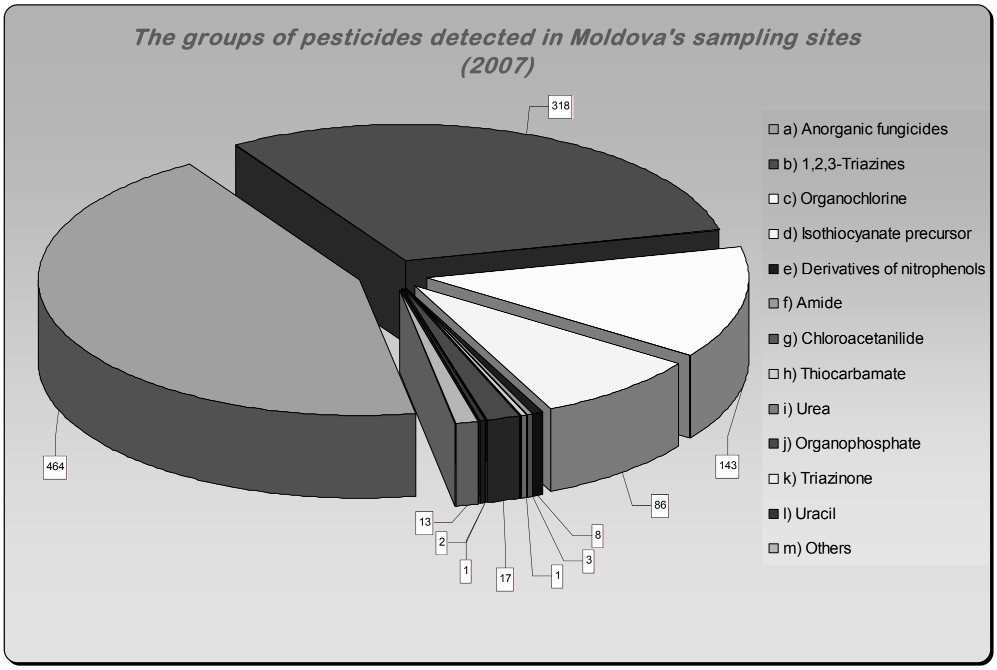
In the republic is implemented, not so fast as it would be desirable, a state program on destruction of obsolete pesticides about 3 thousand tones. The program was accepted in December, 2002. Such preparations, judge by different sources, are available and in some other countries. According to the program at the first phase the inventory of these pesticides is carried out; at the second phase – they are packaged in new capacities, they are assemblage and concentrate for storage in well repaired, protected warehouse premises. These jobs are carried out by the inspectors on protection of plants, Ministry of Defense and Department of extreme situations. At the present the job approaches the end. The third phase is the analysis of the contents of active ingredients and their metabolites, which is implemented by State Centre. Fourth, closing phase is the choice of the safest way of their destructions. And in the final phase – deactivation and rehabilitation of territory of warehouses and other polluted places. In this important job the international experts and structure (NATO), which render the methodical and financial help, actively participate. In particular in the frame of the program: "*NATO Science for Peace "Clean-up chemicals Moldova*" we have received two modern chromatograph: gas GS/MS and liquid HPLC.

The analyses, executed in 2006-2007 by analytical laboratory, are about 3000 samples of pesticides stored in 32 warehouses during a long period have allowed to detect about 60 active ingredients and their radicals. They are grouped in 13 groups (Fig.2) . The greatest frequency of detection was at group 1, 2, 3- triazines-36-38 %. Then with 38-42 % follow inorganic pesticides, specially sulfur containing products. Stable organochlorine make about 8-10%. Along with triazines, which are rather stable, the total quantity of pesticides that are keeping a long time in environment is about 43-47%.

It is known, that Moldova does not make pesticides, and imports them from many countries. Therefore analysis of reference literature has shown that the same active ingredients in composition of various preparations were applied in the countries of Europe and other continents. Taking into account, that each country has the right of a complete interdiction or restriction to application those or others pesticides, then these periods for the different countries are various.

So, from 60 detected active ingredients, from 1970 to 2007 in former Soviet Union and from 1991 in Republic of Moldova have stopped application of 24 preparations. In some countries of Europe, including and the countries of EU before its extension from the same 60 detected active ingredients were forbidden 13 preparations. In Moldova, first of all this interdiction concerns to stable organochlorines, DDT, HCHs, derivatives of carbamine acid (Sevin, Ziram), 1,2,3-triazines and some other.





Thus stopping of application of the stable organochlorine pesticides, triazines, carbamates and some other pesticides, repeated reduction of volumes of their application, high prices for modern means of protection of plants, all-round work on regulated of their registration and the applications, control of the contents in vegetative production by modern devices, very important help on the part of the international structures in destruction of old preparations create favorable ecological conditions in Moldova and next countries, provide reception of safe, qualitative agricultural production.

USE OF PESTICIDES IN THE REPUBLIC OF TAJIKISTAN AND INVENTORY OF POPS-RELATED PESTICIDES

Abdusalim JURAEV

National Coordinator on implementation of the Stockholm Convention on POPs, Republic of Tajikistan

Tajikistan is an agrarian-industrial republic; the territory of agricultural fields is about 901.1 thousand ha, including about 300 thousand ha used for main culture - cotton.

The irrigated fields are used intensively; two harvests of crops and vegetables per year, 5 – 8 harvests of Lucerne is a common practice; also the sub-covering and combined cultures.

In Tajikistan, development of agriculture and, first of all, cotton-growing, is closely connected with use of pesticides for combating agricultural pests, plant diseases and weeds. Agro-climatic conditions of the republic are favorable for quick reproduction and development of many agricultural pests. Besides, the high level of various plant diseases is registered. Agricultural crops are affected by weeds, especially in irrigated zones, where large number of seeds are coming in with irrigation water. It was determined, that potential losses of harvest by low efficiency of protective measures are near 30%.

Before the collapse of the Soviet Union, the republic was related to the regions with intensive use of various agricultural chemicals, including pesticides. Unreasonable large-scale use of pesticides, especially the POPs-pesticides, led to contamination of the environment and breaking of dynamic balance of biosphere.

The serious problem of assuring the ecological safety is non-admission for use of forbidden, obsolete, and unfitted pesticides and their containers. The residuals of pesticides are the source of environmental contamination and the reason of significant negative effects on human health.

The POPs-pesticides, locating in storage facilities, agricultural air-fields and pesticides burial places are of a great threat. However, during several last years, there is no reliable information concerning condition of these objects and volumes of pesticides.

In 2004 – 2005, in framework of the GEF/UNEP Project, the initial inventory of pesticides storage facilities, agricultural air-fields and pesticides burial places was conducted. The first stage of the GEF/UNEP Project was intended to conduct the initial inventory on pesticides stockpiles, which may contain the POPs-related pesticides.

Brief review of pesticides use

Tajikistan has no industrial enterprises for production of chemical plant protective preparations; they are imported from other countries. Till the end of 1990s they were centrally delivered on via the Republican Industrial Scientific Organization (“Tajikselhozhimia”) with full responsibility for appropriate storage, effective use and reliable registration.

From 1965 to 1990, the volume of pesticides delivery to Tajikistan was from 7 to 14 thousand tons (calculated on basis of 100% active ingredients). During this time the volumes of pesticides use changed significantly in accordance with their groups. So, the volume of insecticide-acaricides decreased from 11.1 thousand tons to1.7 thousand tons, but use of fungicides increased from 1,0 thousand tons to 6,1 thousand tons, many fold increased the use of herbicides and defoliants (Table 1).

Pesticides delivery for agriculture of the Republic of Tajikistan
(tons in calculation on 100% of reactant)

Table 1

Name of pesticides	YEARS					
	1965	**1970**	**1975**	**1981**	**1985**	**1990**
TOTAL: **including**	13963	7144	11355	10462	13681	11850
Insecticide-acaricides	11147	2448	1785	2011	2190	1680
fungicides	980	-	2424	2367	6137	4515
protectant	49	33	37	90	420	250
herbicides	105	665	2554	1913	2205	1805
Defoliants and desiccants	995	3140	3490	3982	2667	3450
Others	687	858	1125	101	62	150

The decrease of insecticide-acaricides consumption is stipulated by the decrease of organochlorine pesticides use, the share of which in total volume of used agricultural pesticides decreased 2.7 times in 1989 in comparison with 1965 (Diagram 1), i.e. in figures (tons of reactant) 18 times.

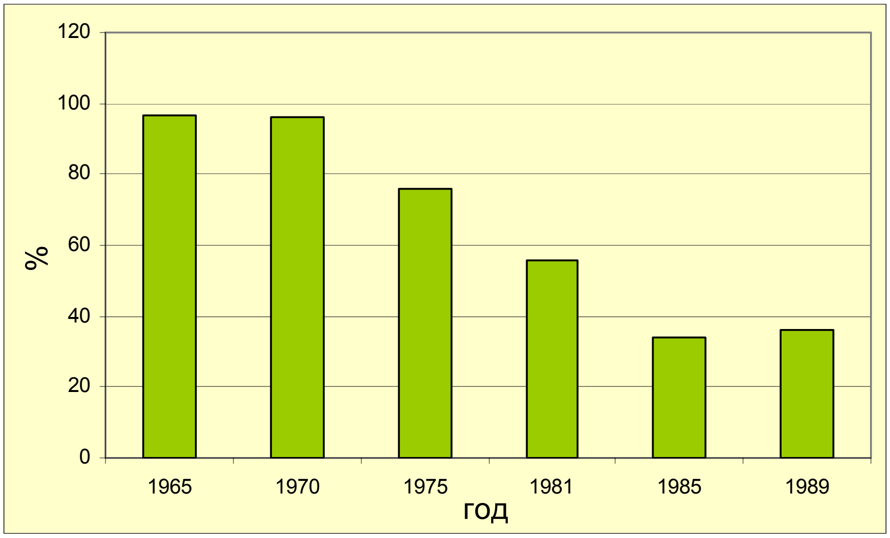


Diagram 1. The share of organochlorine preparations in total volume of insecticide-acaricides, (%).

The assortment of used pesticides included chemicals, which later were considered POPs-pesticides: aldrin, dieldrin, heptachlor, endrin, hexachlorobenzene, toxaphene and DDT. Mainly DDT was used in various concentrations, with an annual consumption from 1960 to 1970 for cotton-growing of 8.7 thousand tons (in preparative form).

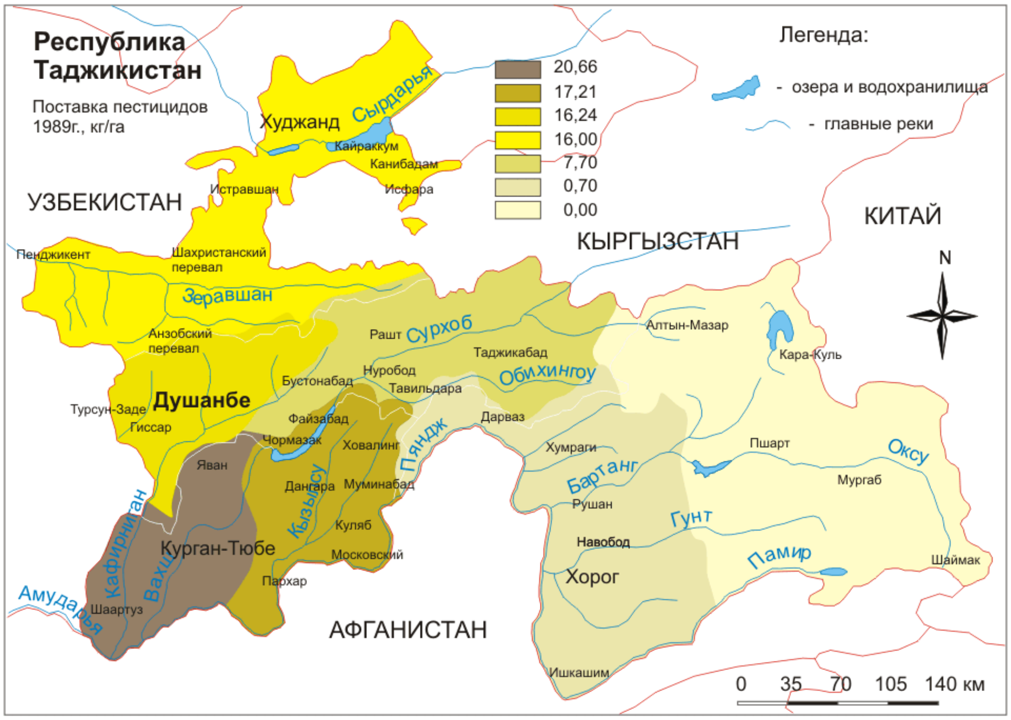
DDT use in agriculture was forbidden in 1970 by Ministry of Health of USSR. The import of other POPs-pesticides was stopped in the middle of 60^{th} years of former century; however, their remainders were used in several consequent years. The maximal pesticides consumption, mainly insecticide-acaricides, was in 1960, and the average figures were correspondingly 18.0 and 14.4 kg of reactant / ha (Table 2).

Pesticides delivery per 1 ha of arable land (kg of reactant)

Table 2

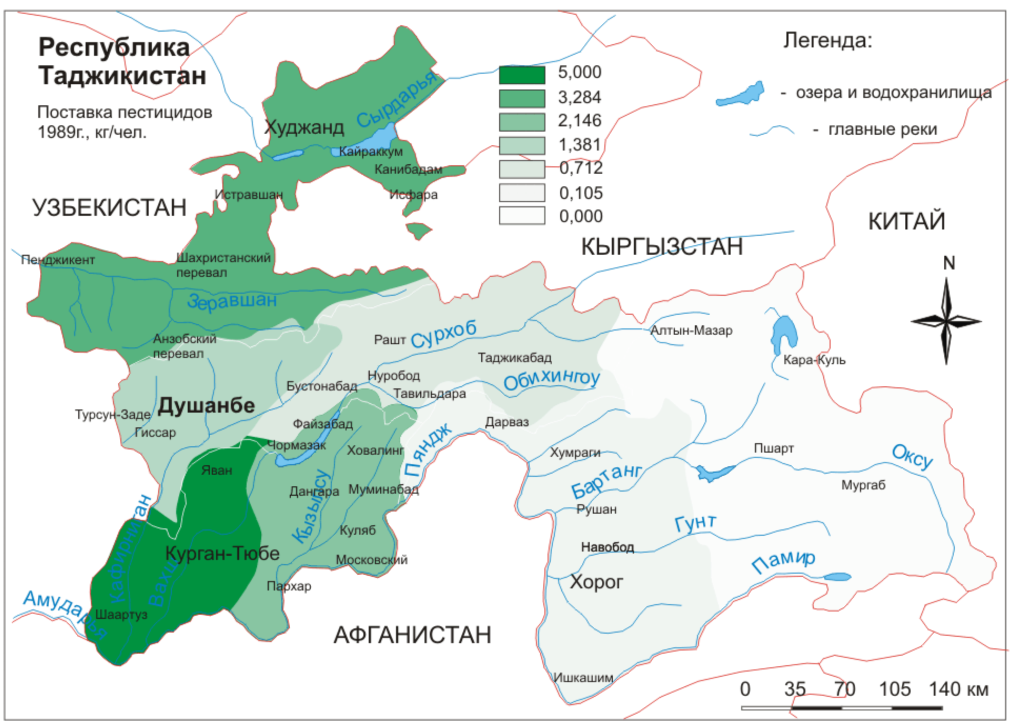
Name of pesticides	YEARS					
	1965	**1970**	**1975**	**1981**	**1985**	**1990**
TOTAL: including	**17,998**	**9,255**	**14,946**	**13,317**	**17,080**	**14,642**
Insecticide-acaricides	14,431	3,169	2,31	2,560	2,734	2,076
fungicides	1,199	-	3,190	3,012	7,662	5,580
protectant	0,064	0,042	0,049	0,114	0,524	0,308
herbicides	0,136	0,862	3,362	2,435	2,753	2,230
Defoliants and desiccants	1,282	4,064	4,594	5,068	3,330	4,263
others	0,886	1,111	1,441	0,128	0,077	0,185

In households of the republic, the pesticides are used mainly on irrigated arable lands (without taking into consideration the hayfields and pastures). Depending on the intensity of their use, on grown agricultural crops and natural peculiarities of the regions the volume of pesticides used varies from 0.7 to 20.0 kg / ha (Map 1).



Map 1. Pesticides distribution per ha of irrigated agricultural lands

The significant differences are observed in consumption of pesticides per capita in rural locations. The highest indicator is recorded in cotton-growing zones (Map 2).



*Map 2***.** Pesticides distribution (of reactant) per capita in rural location

Pesticides were used predominantly on cotton-growing fields. In the republic the average repetition factor was 6 – 10 times and in certain districts of Hatlon region it was even much higher – till 17 times (Table 3).

Pesticides use, including POPs-pesticides, in cotton-growing fields

Table 3

YEARS	Arable lands, thousand ha	Volume of chemical treatment, thousand ha	Repetition factor
1961	204,2	2102,0	10,2
1965	228,0	1700,0	7,4
1970	254,0	1059,0	4,1
1975	271,5	923,0	3,4
1980 - 1985*	306,0	1270,0	4,7
1986 -1990*	313,0	889,0	2,8
1991 -1995*	281,0	645,0	2,2
1996 - 2000*	235,0	408,0	1,7
2001	263,0	518,0	1,9

* - average per year.

The agricultural aviation was widely used for chemical treatment of arable lands; the share of aviation was about 86%. As a result, on densely populated irrigated territories of the republic an intensive process of accumulation of various plant protection chemicals in the environmental components (soils, water, silt, plants and etc) took place. It became a fact of a great concern; and in the republic measures were undertaken for decreasing of pesticides consumption, and in particular: the integrated system for combating pests of agricultural plants was introduced on the base of combined use of all plant protection measures – agro-technical, biological and chemical ones (Diagram 2).

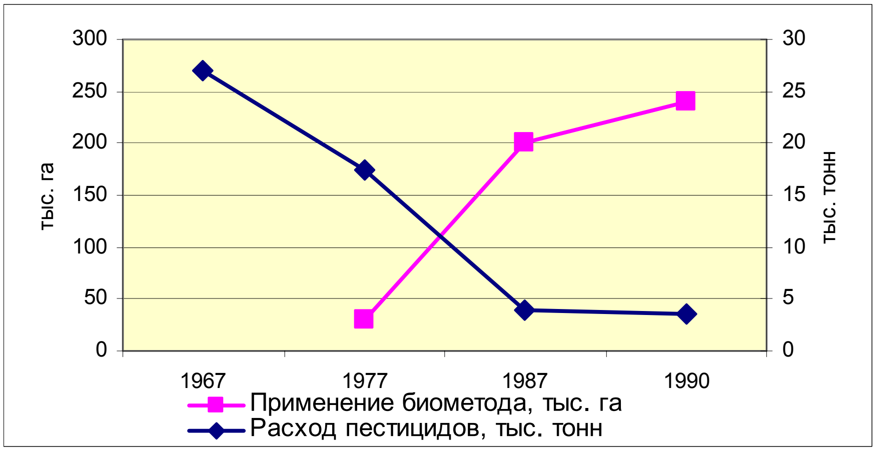


Diagram 2. Use of pesticides and biological method for agricultural pests' control

The important role was given to the improvement of chemical method, determination of selective preparations for elimination of harmful microbes, use of microbiological preparations and entomophages. During a short period a network of biological laboratories was created, and also the biological factory was installed. The chemical treatments were conducted in accordance with the results of their researches taking into consideration the threshold of pests' injuriousness. The volumes of chemical treatments by agricultural aviation were decreased significantly, and the use of land technical equipment increased – it was more an ecologically sound method (diagram 3.) In operative season, in these households specialized teams for agricultural pest control were created.

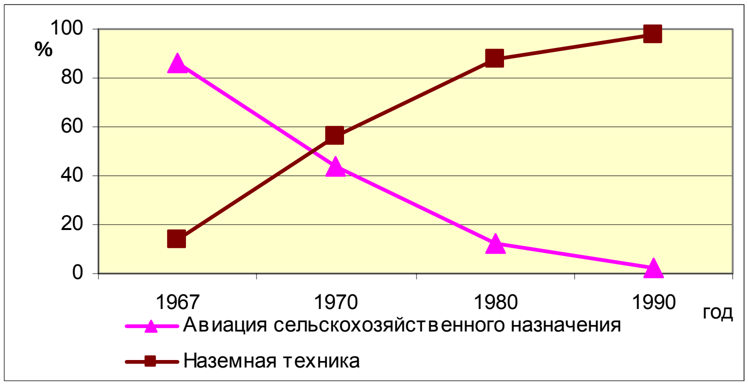


Diagram 3. Pesticides treatment with use of agricultural aviation and land technical equipment for control of pests and plant diseases (% from total volume of work)

After 1991, the pesticides consumption decreased sharply for various reasons (breaking of economical relations, lack of finances in economy and so on). During 15 years, the delivery of pesticides to the republic was about 21 thousand tons. In 2003, according to Customs Service data, the import of pesticides was 135 tons. The factual volume of chemical treatment of crops testifies that pesticides were used much wider. Delivery of pesticides is realized by various firms and private persons, so there are cases of illegal import of obsolete and forbidden pesticides. In 2005 – 2006, Customs Department within Ministry on State Incomes and Taxes of the Republic of Tajikistan revealed and prevented illegal realization of 17 tons of DDT, delivered from a neighboring country, probably from China.

In connection with reforming of the state agricultural system, the quality of reliable reporting of pesticides use and the observation of regulations on their use have been aggravated. The increased number of chemical treatments against pests is ineffective and, at the same time, the contamination of environmental components is observed.

In the light of above, it is necessary to create an efficient system for controlling the import and consumption of pesticides. Besides, it is very important to improve the awareness and professional knowledge of land-users about the harmfulness of POPs-pesticides. Only in this case the situation may be avoided when the benefit from pesticides will not invert to the damage for nature and peoples.

The results of initial inventory of forbidden and obsolete pesticides

Nowadays, the great threat to human health and the environment comes from of the existent obsolete and unfit pesticides. During the delivery of pesticides to the republic it was observed that households' requests were 1.5 – 2 times higher as the real demand. This led to accumulation of great remainders in the storage facilities of the households and bases of Republican Productive Scientific Organization "Tajikselhozhimia". The following factors also contributed to their accumulation:

- prohibition of purchased preparations use due to their toxicity and harmfulness for the environment, issued by health care agencies;
- inefficiency of chemical preparations against certain objects;
- expired shelf life of pesticides because of long-term storage;
- unfit containers, their bad quality and destruction of their covering in the process of long-term keeping;
- unfit preparative form;
- low stability of preparations by their keeping;
- unsatisfactory organization of keeping and registration.

Due to availability of significant remainders of pesticides, their uncontrolled use was observed: pesticides were given to the private persons for use in their farmlands; there were cases of unauthorized burying or deposition at the dumps.

During the last years, due to a sharp decrease of pesticides delivery to the republic, their remainders, including forbidden and obsolete ones, were used.

As a result of conducted initial inventory 17.55 tons of DDT was revealed, including 17 tons of illegally imported in 2005 – 2006 to the southern region. Other 0.55 tons are found in two households of Gissarski district. In the storage facilities, where packaging was destroyed due to a long storage, 42.1 tons of unfit pesticides were revealed: herbicides, protectants, defoliants and sulphuric preparations. In the examined objects more than 100 tons of unknown pesticides were found, causing the anxiety due to great harmfulness for the environment. Especially harmful are the unknown chemicals, lying in the open air near storage facilities, neglected places of chemical solution preparation, and in burial places of illegal digging of pesticides. Here they are exposed to precipitations and wind, which transfer them to long distances.

From 236.9 tons of pesticides, revealed in burial places, the number of forbidden, obsolete and mixtures of unknown pesticides is 160 tons. Moreover, there are approximately 4500 tons of mixtures of unknown pesticides with soil, various substances and garbage (Diagram 4).

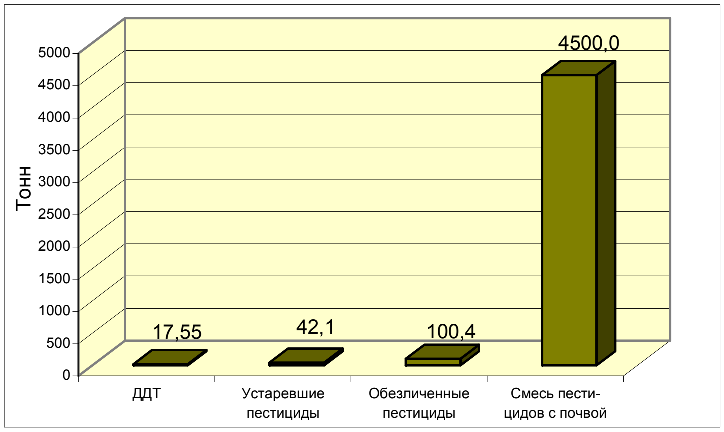
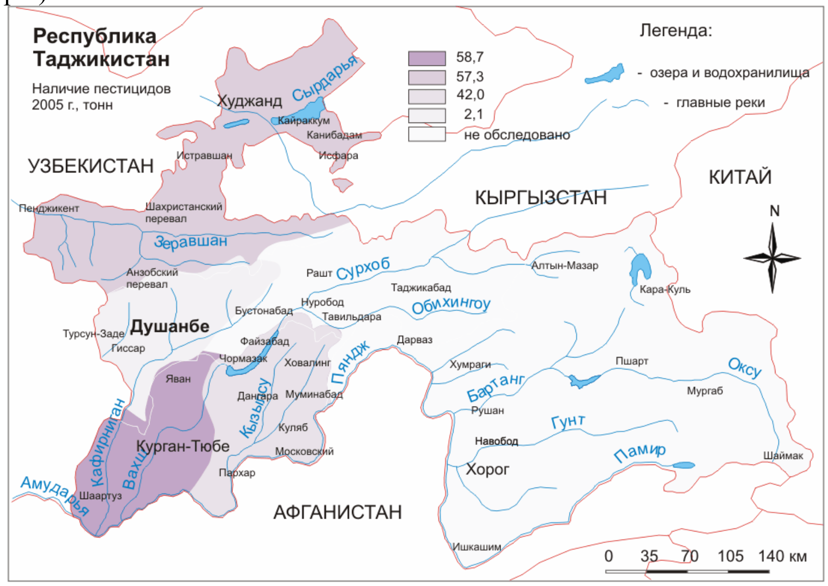


Diagram 4. Unfit (forbidden and obsolete) pesticides and their unknown mixtures, revealed during initial inventory

By conducting a detailed examination of storage facilities and agricultural air-fields all over Tajikistan, the above-mentioned number of unfit pesticides and their mixtures may increase 2 and more times.

Distribution of revealed forbidden, unfit pesticides (including POPs-pesticides) and their unknown mixtures all over the region of Tajikistan confirms the existence of serious threat to human health and the environment (Map 3).



Map 3. Distribution of revealed forbidden, unfit pesticides (including POPs-pesticides) and their unknown mixtures (information on 01. 07. 2006)

Inventory of pesticides storage facilities

Simultaneously with pesticides inventory their storage facilities were examined. These storage facilities were intended only for pesticides storage, but keeping there any other products or incompatible pesticides groups is strongly prohibited. The inventory covered 167 storage facilities from a total of 372 that functioned till 1990. The following facts were revealed:

- all standard storage facilities of former Republican Productive Scientific Organization "Tajikselhozhimia" are privatized; part of them is completely destroyed and materials were used to build new houses and economical objects;
- almost all existing storage facilities of former collective farms are largely ruined; many of them have no roofs and no windows, their roofs are broken; the repair works are not conducted;
- often, these storage facilities have no fencing and guarding; the access for population and domestic animals is free;
- some of storage facilities are located near settlements and economical objects, near water sources, agricultural fields and gardens;
- some storage facilities are used for storing forage, various building materials and household equipment. There are some very dangerous cases where storage facilities have been used as living quarters;
- there is no documentation on pesticides registration in any of existing storage facility.

Due to the fact of unknown pesticides and their mixtures availability in storage facilities, it is necessary to conduct their identification to reveal the POPs-pesticides.

Availability of empty pesticides containers

Serious attention should be paid to the empty pesticides containers, because they pose a great threat to human health and the environment. During the period of intensive use of pesticides, there were a lot of empty containers; however, only few of them – predominantly in unfit condition, were returned to the storage facilities.

Thus, about 30% of 100-200 liters iron containers and about 3% of 30-40 liters aluminum cans and flasks were returned to the storage facility. The paper and cellophane packages were practically not returned. The containers were sent to the pesticides producing factories due to expensiveness of transportation. At the same time, the empty containers were transported from storage facilities to the pesticides burial places, where 50 thousand units were buried altogether.

Containers in proper condition, mainly plastic 5 – 10 liters containers, are widely used by population for storage of drinking water, oils, flour and other foodstuff and other purposes. Unfit containers are thrown away to the dumps of solid municipal wastes and various pits. Cases of peoples and animals poisoning have been observed by using empty pesticides containers for domestic purposes.

In accordance with existing information, nowadays, population uses about 40 thousands containers, 80% of which are plastic containers.

Agricultural air-fields

The main source of negative effects on the environment and population is former agricultural air-fields. Till 1980, in collective farms of the republic altogether 140 air-fields were in function. This includes pesticides storage facilities, water-pits, containers for preparation of process solutions and loading mechanisms. They are divided into permanent (with hard cover) and temporary. Nowadays, none of the air-fields is functioning; many of them are completely liquidated. From 37 examined air-fields, only 13 partly preserved airfields with hard coating were revealed.

Practically all agricultural air-fields with ground lining and majority of permanent air-fields (with hard coating) are used for growing of various agricultural plants; also the pasturing of domestic animals is sometimes observed. All storage facilities within agricultural air-fields are destroyed. Building materials, pesticides remainders and empty containers are taken out by population.

Pesticides burial places

In order to prevent the negative effects of disabled pesticides on people and the environment, the Government of Tajik SSR accepted the Statement No. 104 from 13th March 1970 about allocation of land plots and construction of Vahshski and Kanibadamski for burial and destruction of pesticides.

Pesticides were buried and sometimes burned here. During 1973 – 1991, about 3000 tons of pesticides were buried in Kanibadamski burial place and 1000 tons of bio-preparations. The majority of buried pesticides relates to persistent organic pollutants.

Nowadays, the condition of this burial place is extremely bad, and it is a great problem. Lack of fencing and guarding in pesticides burial places made them accessible for local population and domestic animals. The sluice, built in former time in this burial place for collection of rain and mud-torrent flows, is destroyed. It contributes to contamination of located below territories with pesticides, in case if they will be washed down by precipitations.

Pesticides were buried and sometimes burned here. During 1973 – 1991, about 7500 tons of various pesticides, including about 3000 tons of DDT were buried in Vahshski burial place; in Kanibadamski burial place - 4000 tons, including 1000 tons of biopreparations. The majority of buried pesticides are POPs pesticides.

Nowadays, the condition of this burial place is extremely bad, and it is a great problem. In the last years there their guarding system was liquidated, also, there is no any control of their functioning. Lack of fencing and guarding in pesticides burial places made them accessible for local population and domestic animals.

Presently, due to a great deficit of pesticides, the local population illegally digs out these pesticides, including forbidden ones, from the burial places and sells them under various names. Extraction of buried pesticides is realized both by hand and by technical equipments; the great scattering of pesticides, leading to contamination of burial place's territory, is observed. All over the territory the empty metallic and plastic containers are lying around.

High temperature during summer period and intensive solar radiation contribute to decomposition and evaporation of pesticides, and repeated winds of local origin, and often wind-storms are spreading of objecttionable odor and transmission of harmful substances to the significant distances.

The results of laboratory investigations showed, that in samples of soils and pesticides blends, taken in excavation plots of burial places, there is a lot of various pesticides. In Vahshski burial place, the volume of all pesticides in such samples is from 11606 mg/kg to 40288 mg/kg. Availability of DDT and its metabolites is 79%, and HCH-isomers – 36% from total volume of revealed pesticides. In all tastes samples were revealed such pesticides as eptam, lindane, dinoseb, HCB and teodan, and in some of them – prometrin and dursban; availability of preparation with POPs-properties is in the limits from 7372 mg/kg to 23921 mg/kg.

In Kanibadamski burial place, in the samples of pesticides-and-soil mixtures, taken in unturned plots, the sum of all pesticides varies in the limits of 2195 – 31831 mg/kg, including POPs-pesticides: from 327 mg/kg to 8024 mg/kg; the share of DDT and its metabolites is from 17 to 35%, and HCH isomers – from 3 to 13% from total amount of pesticides. In the majority of samples (85%) dieldrin from 0,05 to 1,14 mg/kg, HCB, eptam, ovex, akrex and dursban were revealed.

Availability of POPs-related pesticides in the objects of inventory

For chemical identification of unknown pesticides and revelation of POPs, 264 samples, including 111 samples of unknown pesticides, 143 samples of pesticides and soils mixtures and 10 samples of soils, were sent to Bashkir Republican Scientific Research Ecological Center (Ufa city).

The results of laboratory analyses showed presence in all samples of unknown pesticides mixtures DDT and its metabolites (from preparations with POPs properties).

In samples of pesticides and soil mixtures mainly the DDT and its metabolites, and also aldrin, dieldrin, endrin, HCB and heptachlor in small quantities were revealed. It confirms that the POPs-pesticides were used in former time in Tajikistan.

The availability of unfit and forbidden pesticides, their broad distribution, possibility of free access to them, high risk to population and the environment, especially in cases of natural disasters, calls for an immediate destruction of such chemical substances.

Conclusions and recommendations

1. The results of conducted inventory allow understanding of obsolete pesticides problem, revealing of forbidden and unfit preparations, including their number, assessing the technical condition of storage facilities, agricultural air-fields and pesticides burial places; all this is necessary for stopping of negative pesticides' effects on human health and the environment. However, more accurate results of the inventory are required to solve the problem.

2. In the examined storage facilities 160.1 tons of forbidden, unfit pesticides and unknown blends, including 17.55 tons of DDT were revealed. Moreover, in storage facilities, on adjoining territories and in places of pesticides solution preparation there were revealed the blends of pesticides and soils in amount of about 4500 tons.

3. Almost 70% of unknown pesticides and 37% of their blends with soil are identified, in pesticides mixtures DDT and its metabolites (from POPs-related substances) were revealed. In pesticides and soils blends,

together with DDT, there were revealed aldrin, dieldrin, HCB, endrin and heptachlor. It confirms that in former time these preparations were used in the great volumes.

4. Almost all pesticides storage facilities are in bad condition; often, they have no fences and are not guarded; some of them are located near settlements, water sources and agricultural fields. Some storage facilities are used for other purposes, such as granaries, storehouses for building materials, household equipment and etc.

5. Also, the major problem is the unsatisfactory technical condition of Vahshski and Kanibadamski pesticides burial places. Nowadays, these objects are neglected; that is why, they pose a threat both for human health and the environment;

6. To prevent the negative effects of pesticides burial places it is necessary to eliminate the buried pesticides and rehabilitate these land plots together with adjoining contaminated territories.

7. In the republic, the empty containers are still accumulated, and the population keeps using them for domestic purposes. Nowadays, more than 40 thousands of empty containers are used by population, and more than 80% of them are plastic containers of various capacities, which cannot be buried or burned in the open air.

8. Conducting of detailed inventory in all agricultural regions of the republic will allow collecting reliable information about the quantities of forbidden and obsolete pesticides, which should be destructed.

9. It is necessary to determine the measures for rehabilitation of pesticides burial places and contaminated territories with taking into consideration the ecological risk, economical and technical possibilities.

10. It is necessary to conduct laboratory analyses, to determine the pesticides residuals, especially POPs-pesticides, in environmental components and agricultural production, and to arrange the appropriate control of imported pesticides.

11. The regulation of pesticides use is also of a great importance; for its establishment it is necessary to arrange an effective reporting and controlling system of their import and use by means of strengthening of legislative framework in this field.

It is necessary to assure the public awareness raising process concerning harmfulness of pesticides, and in the first line the POPs-pesticides, for human health and the environment by means of publication of popular-scientific articles, brochures, placards, etc.

COMPLEX PERFORMANCES OF THE CONTEMPORARY PERSONAL PROTECTIVE CLOTHES

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Not a long time ago we were the vitness of more chemical accidents. This fact is also is important because we are the crossroad of numerous important European communications, where a lot of such transports are passing by. Great number of these substances can hardly damage human environment for a very long period of time. The new personal protective equipment (PPE) offers the opportunity of substantial cost savings by eliminating the need for additional, expensive over garments, whose high weight and poor breathability may also cause a physiological overload of the user. This work studies such events according to different parametars, trying to find the way how to successifuly prevent them and protect against this threat.

Key words: chemical protection, pesticides, personal protective equipment

Introduction

During the 1990's, the concept of the NATO modernization introduced the requirement to equip soldiers with a combat clothing system with fully breathable integral nuclear, biological and chemical (NBC) protection. The advantages of such system are:

- reduced heat stress,
- reduced weight and bulk of protective equipment to be carried,
- increased operational efficiency of the soldier in an NBC environment,
- reduced costs.

Since the World War I, when chemical warfare agents were employed for the first time in large quantities, the protection of soldiers has been an ongoing challenge for research and development personnel. Alongside gas masks that protect against respiratory agents, impermeable rubber suits represented the first body protection. Unfortunately these suits have major drawbacks: they are complicated to don, create high-heat stress for wearers and are vulnerable to unsealed openings and/or damage, so the development of permeable protective suits began in the 1960s. In this type of garment, hazardous gases are removed from the air by means of adsorption conducted by filter fabrics containing activated carbon. Textile filter fabrics of non-woven or polyurethane foam are loaded with activated carbon powder. Other technology use a carbonized and activated woven or knit fabric fixed onto a textile carrier. In figure 1. are represented an A, B, C and D levels of chemical protection. In the level D we have any type of coverall - in this case it is Tyvek from Dypont, chemical protective gloves and resistant safety boots. In the level C we have protective overall, protective mask, rubber boots and chemical tape for additional air-tightness. In the level B we have liquid-splash protective suit in combination with self contained breathing apparatus. In the level A we have fully encapsulation with vapor protective suit.

Figure 1. Chemical protection levels

The modern concept of filter sorption materials consists of a coat and trousers (figure 2). The coat features a full-length zippered opening covered by single protective flap, an integrated hood, hook, and pile sleeve closures. The trousers feature adjustable waist tabs, suspenders, and closures on the lower outside section of each leg. The suit can be worn over the duty uniform or undergarments. The suit is wearable in all environments and conditions and is compatible with the gloves, boots and mask. It is not degraded by fresh or salt water and is launder able. The outside layer of material is cotton rip stop that has been corpel treated.

Figure 2. NBC clothing including Saratoga™ suit

The characteristics of textile protection materials

The Saratoga™ material has a high flexibility, high air permeability and a low thickness, which together provide very high wearer comfort. The two layers and the air gap provide comfort and efficient heat control of the body under all climatic conditions. The suit employs spherical carbon technology to provide effective body protection from well-known chemical/biological warfare agents while offering the best possible flow conditions for body heat dissipation, so that the suit stays as cool as possible. The activated carbon provides additional protection against chemical warfare agents in liquid, vapor and aerosol forms (figure 3.). The latest and most successful technology, developed by Blücher GmbH/Germany under the brand name Saratoga™, offers the highest capacity of adsorption and the best possible comfort under all climatic conditions. Saratoga™ is based on activated carbon in the form of spherical absorbers that are fixed to a textile carrier fabric. The capacity to adsorb CW agents by activated carbon is defined by the characteristics of the porous system, the level of activation and the amount of carbon. Saratoga™ is unique patented composite filter fabric based on highly activated and hard carbon spheres (figure 4.) fixed onto textile carrier fabrics [1]. With a carbon density of between 180 g/m² to 220 g/m², the maximum on the market, it provides a minimum of 24 hours protection and at least 45 days of wear under battlefield conditions, including several field washings. Over 85 % of the sphere's outer surface is freely accessible to harmful gases, resulting in an extremely rapid and firm adsorption.

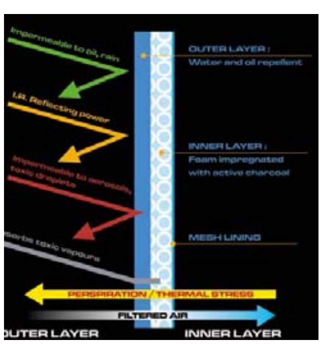

Figure 3. Layers of filter sorption material

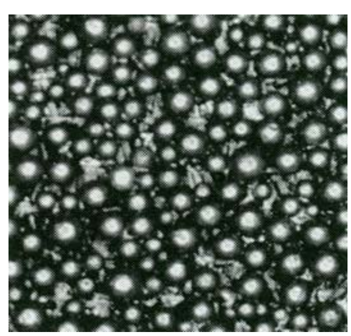

Figure 4. Active charcoal spheres

The level of activation also is important for desorption (the release of adsorbed gases) because desorption of CW agents could threaten wearers as well as unprotected personnel. It has been proved that when using carbon beads CW agents desorb only above 100 °C and in concentrations above the non-effect level [2]. Therefore CW agents are trapped safely within the beads. Rubber suits do not offer any adsorption capacity, they are simply impermeable barriers for CW agents. Semi-permeable membrane materials that have been under research for many years, are airtight, as are rubber suits, but designed to be permeable for water vapor molecules to evaporate from the skin. Unfortunately, the barrier properties of CW agents makes them inferior to rubber. Evaporating water molecules can be adsorbed by the membrane for transport to the outside, making the membrane swell to create enough space for larger molecules, such as CW agents, to pass through. The lack of adsorptive properties in rubber and membrane suits means that these types of suit have to be completely sealed from the environment. It is almost impossible to avoid damage to a suit during field use and equally impossible to close all openings perfectly because movement in the suit will alter internal pressure and create airflow. Any CW agent penetrating through openings or even slight damage will be resorbed by the skin from air inside the suit. In Saratoga™ permeable suits, the adsorptive power of the carbon beads is higher than resorbtion of skin, so the carbon beads remove CW agents from air inside the suit. Another important criterion is wear comfort or heat stress. Permeable protective clothing was designed so that evaporated sweat may be transported through the filter material and small openings by the air stream created by the wearer's movements. In rubber and membrane suits air stream has to be blocked completely, therefore no transfer of sweat from the inside to the outside takes place because there is no air stream and no transport through the material (1). Membrane suits also do not facilitate air stream but do allow a limited transport of sweat through the material (figure 5.). Only permeable suits based on activated carbon technology offer efficient heat and sweat transport through fabric by ventilation [3].

$$M - W = C_{res} + E_{res} + K + C + R_a + E + S \qquad (1)$$

C_{res} and E_{res} are heat exchange in the respiratory channel by convection and evaporation K, C, R_a i E heat transfer by conduction, convection, radiation and evaporation and S acumulated heat.

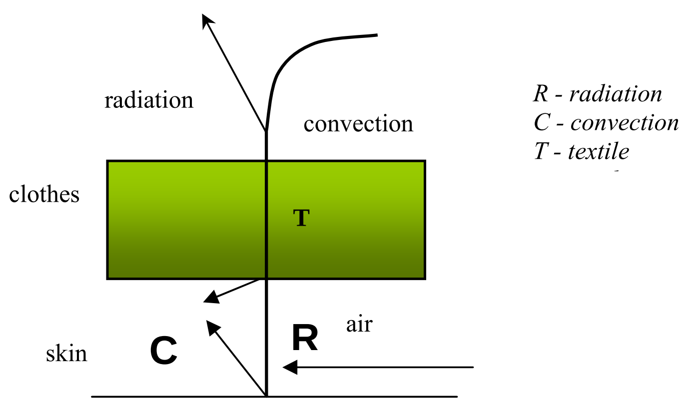

Figure 5. Exchange of dry heat in the clothes

The Saratoga™ system, with its high-capacity carbon beads, offers active sweat management and thus highest wear comfort. Saratoga™ NBC protective garments can be worn under all climatic conditions with minimal impact on combat effectiveness. The better the wear properties of a protective suit, the longer it can be worn for preventive protection without fear of serious loss to operational strength. The microclimate between skin and clothing has a great influence on the wearing properties. The pore structure of the Saratoga™ spherical absorbers and their hydrophilic properties have the effect that sweat impulses are caught and continuously decomposed. This causes a low increase of humidity and a low atmospheric humidity in the area very close to skin. For that reason Saratoga™ is pleasant to wear. The high flexibility of Saratoga™ filter materials leads to a "pump effect" which increases the microclimate such as a quick exchange of the air in between the inner and outer textile layers. The suits are also highly air permeable meanings that sweat and heat stress are reduced [4].

Experimental

Saratoga™ has a very high mechanical stability. Due to excellent mechanical properties, can be used for training purposes; after being washed and packed, the protective suits are fully suitable to be re-used. In this investigation ten people were tested in the climatic chamber. The temperature was 30 ºC, relative humiditu 50%. During the 90 minutes, they walked at 5 km/h velocity.

Figure 6. Testing in the laboratory

Figure 5. Working on primary missions

After laboratory testing, we're realized primary missions in the field using this overgarments. The tests are realized in different enviromental protection [5]. In several laboratories are tested physical-mechanical, functional characteristics and resistance of materials (inner and outer layer) on influence of high toxic chemical substances [6]. The main characteristics of suit material (inner-filter and outer layer) are given in tables 1 - 3.

Physical-mechanical textile properties

Table 1

Thickness, mm	Before treatment		After climatic treatment and use	
	filter	outer	filter	outer
Thickness, mm	0.79	0.41	0.78	0.4
Breaking strength, daN	65.3	99.4	61.7	96.2
Tearing strength, daN	10.7	14.1	8.9	12.5

Functional properties of textile material (sandwich)

Table 2

Thickness, mm	Before treatment	After climatic treatment and use
	filter + outer	filter + outer
Air permeability, Pa	17.4	14.8
Moisture permeability, $g/m^2 24$ h	3375	3360

Resistance to chemical agents (mustard)

Table 3

Sample	Penetrated amount, μg/cm^2 in 24 hrs			
	1 μL dropsize	1 μL dropsize	1 μL dropsize	2.76 μL dropsize
1	0.1	0.8	0.72	0.11
2	0.08	0.11	0.38	0.38
3	1.75	0.08	0.1	0.16
4	3.2	3.23	0.11	0.12
5	0.13	0.12	0.11	0.13
6	0.63	3.28	1.72	0.13

Conclusion

A filter material show good results on the Milspec tests, showed in tables 1 - 3. From the results given in table 1 it can be concluded that textile materials, which are embedded in this suit, have a lower amounts of physical-mechanical properties after climatic treatment and practical use (wearing in different climatic conditions). From the results given in table 2 it can be concluded that these materials have inferior values of air and moisture permeability after climatic treatment and practical use. The laid drop test (8 × 1 μL) using a mustard agent showed a large spread of penetrated amount. All results were still good enough. From the given characteristics of suit (clothing) material based on Saratoga™ inner (filter) material, it can be conclu-ded that these materials have excellent mechanical, functional properties and resistance to different chemical agents, which makes that new class of protective clothing are very acceptible and necessary in human and health protection in accident situations, war and terroristic actions with chemical and biological agents. In most of these characteristics, new clothing, including inner Saratoga™ layer, are much better than old protective clothing based on PUR/textile materials and rubber materials.

What is more important than humanity? Let's protect people as much as we can! Shall we?

References:

1. Kissa E., Capilary sorption in fibrous assemblies, J. Coll. Interface Sci., 1981.
2. Ellingsen F., Karlsen J., Transport mechanisms through a porous membrane and the subsequent effect on the protection when incorporated into multilayer clothing, Proc. Int. Symp. Protection Against Chemical Warfare Agents, Stockholm, Sweden, 1983.
3. Mecheels J., Klima-Kleidung, Grundzuge der Bekleidungsphysiologie, Berlin, 1991.
4. Umbach K. H., Hautphysiologie und Kleidung Bekledungsphysiogiches Institut Hohenstein, 1978.
5. Karkalic R., Popovic R., Complex perfomances of the contemporary textile materials covered with active charcoal, VI Međunarodni kogres YUCOMAT, Herceg Novi, 2004.
6. Optimization of thin layered active charcoal sorption materials embedded into the NBC protective materials in the function of protective characteristics and physiologic compliance, Radovan Karkalic, PhD, dissertation, 2006.

ENVIRONMENT PROTECTION AND CHEMICAL ACCIDENTS IN THE PESTICIDES PRODUCTION FACILITIES

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Not a long time ago we were the witnesses of a number of accidents that included dangerous chemical substances during the transport. This fact is also important because we are the crossroad of numerous important European communications where a lot of such transports are passing by. Great number of such substances can seriously damage human environment for a very long period of time. The risk is defined as a product of a failure probability and its consequences. This work studies such events according to different parameters, trying to show the way how to successfully prevent them and protect from this threat as in the peace time, such as during the war operations. At the time when dangerous substances are transported we usually don't have the valuable information about everything we need to know to prevent it. The emphasis of the paper is on chemical risks caused by structural failures leading to the serious involving pressure wave, flames, explosions and toxic contamination in the pesticides production facilities. So, realization of the universal and united system of NBCD gives us a possibility, using modern communication equipment and very effective mobile units, to react in a real time and successfully perform monitoring, alarming, protection and decontamination.

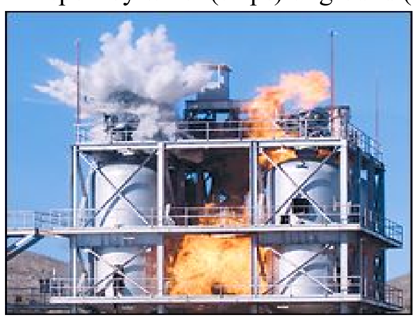
Key words: human environment, risk, chemical accident, pesticide, contamination, risk management, monitoring, protection, preventive measures, decontamination.

Introduction

Chemical accidents are damages of production plants or damages that appear with toxic, flammable or explosive substances. Impacts happen suddenly and without control, so most of the liquid, evaporation or aerosols release in long term of time. Contamination of objects, atmosphere, and soil occurs with consequences for humans and nature. Uses of chemical weapons in war, chemical accidents in peace and terrorism have similar characteristics of effects and consequences on the nature. Differences reflect in diversity of chemical compounds, their amount, dangerous concentrations, big range of effect, difficult identification etc. By analyzing past events of chemical accidents we can say that they were divers with heavy consequences on human population. Chemical accidents mostly happen in facilities of production, but they also happen in car accidents (distribution of dangerous chemical cargo). In the case of heavy accidents many hours and days had past before population received warning about potential danger. Reactions of accident in a country appeared with delay so the consequences were higher. Many facilities have great amounts of toxic substances which are raw materials or final products intended for peace or war purposes. Causes of chemical accidents lie in fire, explosions, and uncontrolled turbulence of toxic material in atmosphere, water and soil. They occur because of old technology, "higher force", negligence, disrespecting proper form of protection, diversion, sabotage, terrorist actions etc. In war in conditions of chemical weapons usage, terrorism and conventional weapons, number of chemical accidents with enormous consequences would be great. A problem is present in the case of chemical accidents, that they are discovered much too late or never and that the cause of accident is never discovered, many of them happen during the night and in series. Chemical accidents can happen in multiple ways, explosions, terrorist actions, war impacts, old technology, disrespecting proper form of protection etc. By that, vast amount of toxic material goes to atmosphere and in the soil and it can be very dangerous to plats and human population. As chemical facilities are often located in urban surroundings, accidents present great danger to human and nature. There are many significant industrial objects for pesticides production and stockpiling in Balkan, with various technologies, complicated warehouses and difficult transport. Transport of harmful and dangerous material goes through air, by see or river, by railroads and highways, through pipelines and other sorts of transport. That is very much alike human blood veins and it can be easily compared.

Characteristics of chemical accidents

Damages in stationery objects are all damages in production facilities, storage rooms and pipelines in production system. Basic characteristic is that every possible location of damage is known. The problem is that we do not know in advance when damage will occur. Next characteristic is also familiar, all kind of chemical substances that can leak out are known. They are being determent by the sort of technology. Only if they change, which does not happen very quickly, the number and sort of dangerous chemical substances will change. Taken this into consideration we must take care of amounts of substances, because they change during production, which depends on dynamics of supply, production holdbacks and other. However, from the point of environment protection, that is, necessary measures for damage sanitations it must be taken into consideration the number of chemical compounds that are being used so as the amount that is being stored in a facility. Only then safety measures can be predicted to eliminate consequences. When we speak about sorts of chemical substances, and their amounts, we should emphasize that there are more than just those that go through chemical process, but also the substances that appear as side products or inter products in production process and that they can in a case of damage be relished into the surroundings. Chemical accidents represent suddenly and uncontrolled release of dangerous and harmful material into the surroundings. Fire, explosions, high pressures and burst of contaminators cause great material damage, victims, destructions and degradation of nature for a long period of time with enormous consequences. Damages in non stationary objects are those that happen during the chemical transport by water (ships) or ground (railroads and automobiles) transport [1].



Picture 1. Chemical accident in a facility

In case of industry accident, there would be an occurrence of explosion or so called strike of fire ball, fire and uncontrolled appearance of contamination, which would lead to sudden appearance of toxic clouds, evaporations and aerosols. By keeping that in mind, accident in a chemical facility could be classified in four levels of danger [2]:

***I Level (local)*:** effects would be limited only to facility, warehouse, and industry in which the accident would happen. For its control and sanitation would only be required local means and forces.

***II Level (city)*:** effects would affect a wider territory and it would require forces and means of the city to control and sanitize the accident.

***III Level (regional)*:** this means an accident in a big territory whose effects are of regional significance. Control and sanitation would require joint local and regional forces.

***IV Level (interregional)*:** accident is of interregional proportion. For control and sanitation are required special mean and international aids.

Management of protection quality

By perceiving all of this elements of potential chemical accident and their mutual influence we come to conclusion on which protection of population, units and facilities is being made. Security measures against NBC accident is monitored by the orders of commandant of the garrison (airport-seaport) in cooperation with police force and persons responsible for local community. Orders for security measures have a cause of security, assignments, forces and means, warnings, alert, measures of chemical protection, ways of a region evacuation, forces and ways of engagement in security assignments, accidents control, removing the consequences, logistics organization of command and connections In order to effectively response to chemical accidents in these conditions it is necessary to define and form adequate forces for completing assignments for security measures - protection of environment. In the form of program assignments it is necessary to define a unique CBRN system (constantly on duty and mobile), to prevent or lower consequences of chemical accidents, followed by leaking of chemical substances into the environment. In the form of AIS environment protection there should always be data (with what crew, work teams are specialized for high professional work with certain groups of chemical substances) for sanitation of accidents consequences and other damages. It is also needed the modernization of means and equipment, especially for conditions of security – protection from nuclear and chemical accidents in peace. It is necessary to train personnel, that can effectively respond to go there and chemical accident in peace. In this paper we're not discussing the causes of social, ideal, material or other aspects but we're facing the fact that in that cases the information as were late. Causes were different: human factor, technological factor, late discovery of danger, fear of consequences and responsibility, political reasons and other. Discovery and following of distribution of contaminated cloud after the chemical accidents is possible to monitor with half empirical model. In this case, in the zone of accidents the primary cloud of contamination appears by steam release, gases and aerosol poison after which by the influence of whether is being distributed to certain distance. Larger dispersion systems first of all contaminate the ground and objects, and then evaporate and form secondary contamination [3]. Most chemical facilities, especially those with intent and production carry in self certain risk in the process of production and material distribution. Therefore it is necessary to constantly monitor and prevent, on scientific basis, chemical accidents. Most of the world countries can't great importance and insist on readiness in case of chemical accidents, and deceive to form international body for safety of modern technologies. In this way, it is required the responsibility of governments that do not take certain measures of protection on work and do not inform international community about danger, that can happen.

Plan of security of chemical accidents in these is being worked on the level of production, garrison (airport, seaport) of military region and county. By this plan is being enveloped all the essential interests for the organization of security activity with which are being made conditions for live and work of units (facilities) in the case of accident. Plan of security consists of danger evaluation from an accident, conclusion from estimation and orders for organization of security. With these documents there also other essential documents that provides better organization of security (men with the preview of element estimation, when of forces engagement, directions for teamwork, plan of connections and other). Basics of the plan are being made by an evaluation of danger from the accident and the quality of information will depend on the quality of security and protection of the environment. The evaluation of an accident is a process in which is constantly monitored the condition and changes of threat in objects and settlements in the zone of responsibility and it consists on: evaluation of source of the danger from the accident, evaluation of threatened and units and objects, evaluation of territory, evaluation of whether and climatic conditions, forecast of primary and after stricken regions, evaluation of consequences of accidents and other. In the form of this estimation the number of production facilities and other objects are being defined, their position in correlation of vital objects and facilities and the type and amount of dangerous substances on disposal. Data about facilities and other objects which are occupied by production, processing, transport and other activities and in connection with dangerous materials are very important and they are the basics of other estimations. These data are received from the authorized county parliament and the data about the activities with dangerous materials from the code of processing. Data can be compared with the data from the, communal inspection, that is, inspector for protection of environment. The same time we get data about sort and amount of dangerous material. Based on the data, a list is being made of the production facilities that handle dangerous material by using the code book that defines the risk of accidents and planning of measure to eliminate consequences when the dangerous material is present in the amount equal or higher than listed in the "book of dangerous material after which a cadastre of dangerous material is being made. All of unnamed material is defined by the code book. It is important to say that the possession of chemical material does not present a potential source of danger. Therefore, who will be the potential source of danger and go into the cadastre of potential source is being decided according to sort and amount of material they possess. In the code book the procedure is defined when in one place are more of materials, that is, when one material has, at the same time, properties of more sorts of dangerous material. For every material from the cadastre are being determent its properties. These data are relevant for the sort of means for protection, solution for decontamination, dimensions of the region's and other. The most significant data that must be known are: name of the material, manufacturer, and year of production, quality, and package. About physical properties we should know: state of aggregation under normal circumstances, color, scent, temperature of melting on twenty degrees, air density. Most important chemical properties are: molecule weight, empirical and structural formula, reaction capability (moister sensitivity, oxygen sensitivity, possibility of the decontamination, reaction with acids and bases and flammability and properties of decontamination). Maximum of three amounts during the chemical accident is being estimated by the fact mother in:

- Ideal models, which suppose that the surface of horizontal cut of the container is constant, that the material is released from a hole in the wall, that it is not two phase system and the they're no resistance during the release,
- Real models, which regards the phenomenon of friction,
- Two phase models, which regards the quality and the specific volume of the mixture of evaporation and liquid,
- Models that regards sudden burst of liquid, gas and steam. In this part of estimation data is being determent according to manual. Also, it is estimated the position of the potential source of danger if an accident might happen during the transport of dangerous material [4].

By that the data is being established about the communications with which transports is being made, distance of communications between objects, azimuth, sectors in which the possibility of an accident is greatest, relative difference of height, natural and artificial obstacle between source of the danger and threatened objects. On the basis of all these data the cadastre of potential source of danger is made. And the map (codebook predicts proportion of 1:500 to 1:10000) the source of danger is being marked: industrial objects, warehouses, transport and means on communications. On the map is also being marked the izo-lines of specific concentrations of gases, aerosols and solid particles of dangerous material (in g/m^3 or mg/m^3) for concentrations that cause death for momentarily death, that are dangerous for people unless immediate evacuation is performed, that can be harmful to shield of people if exposure last more than 30 to 40 minutes, which are determent as different concentrations that are taken as the top value of a emission. By calculating the range and concentrations, the most negative weather conditions are being taken, obstacles between source of danger and threatened objects, the most possible wind direction, objects that channel movement of the clouds with dangerous material (streets, heights, valley's and other). Besides that, on the map is being marked the limitation of the zone and objects that are threatened, then units of civil protection, department for observing and information and other). It is important to say that it can be influenced to lower the danger. Endangered units or object are estimated on the basis of the probability of accident and the possible consequences, by which it is determent in the risk is acceptable. Acceptable risk that can be managed under certain circumstances is foreseen by regulations and activities. If the risk cannot be managed under certain circumstances it cannot be accepted. The risk quantifies as minor (I), little (II), medium (III), large (IV) and very large (V). Risk qualifies on the basis of accidents and possible consequences [5]. By estimating the territory we perceive all of her elements, which influence the appearance of the accident, spread and behavior of chemical effects, engagement of capacity of territory through solving problem of control protection and elimination of conesquences. In addition to that, we estimate the micrographic and urbanity characteristics: settlement and surroundings, relief map, cover, communications, and the especially natural and artificial obstacles between sources of danger and objects. After that, it is estimated at the possibility of evacuation, as the directions for evacuation. Use of computers for monitoring the spread of contamination in atmosphere, time to response on the accident is significantly lowered and this is of the great importance. On the basis of seeing possibilities we come to conclusion about necessity of actions in control, protection and removing the consequences. By perceiving all these elements of estimation from the potential accident and influence we come to the conclusion on which is planned and performed the protection of the population and security of units and facilities from NBC accident periods security from accidents in these is being regulated by the orders of the specific institutions and the president of the county.

Conclusion

Big risks in production, transport, archiving and use of dangerous and harmful substances to life and health of people, animals and plants lies in possibilities of chemical accidents in peace, direct war danger. Analyzing previous chemical accidents in the world and here we can say that there were many, mostly by surprise, with hard consequences for human, animal and plant world. Defense system should unite all parts of the present forces, means and objects, in the form of one unique NBCD system (military security, office for observance and information, civil defense and protection). In the system should be included specialize teams of chemical industry facilities. Basic part of the system should be office for observance and information which can manipulate with all data about substances that are being transported, their destination and other relevant data. For an effective answer to accident in peace, in current conditions, it is necessary in form of organization-formation changes and further enlargement to the find and form adequate forces for completing the special assignments in the form of security in these and defense in war conditions. It is necessary, also, modernization of means and equipment and training the personnel, which will be in the condition will effectively respond to accident in peace. It is necessary to have a unique response unit, highly trained and prepared for eliminating the consequences of an accident in peace, informed of environment protection on the territory of our country. Planned activities of society from accidents in peace (prediction, organization, conduction and control of life security measures) are real and only way to prevent, control, protect and effectively eliminate consequences in all conditions.

References:

1. Markovic D. Osnovni procesi i stanje u zivotnoj sredini, Univerzitet u Beogradu, 1997.
2. Biocanin R. Protection of the human enviroment in case chemical accident, II regional simposium "CHEMISTRY AND THE ENVIRONMENT" 18-22. june 2003. Krusevac.
3. Amidzic B., Biocanin R. Ekološki menadžment u funkciji zaštite i unapređenja životne sredine, IV Medjunarodna konferencija " SyмOrg 2004", 06-10. june 2004. Zlatibor.
4. I.Burton, "What happened at Mississaga", Planning emergency responce system for chemical accidents, Adminitrative Guidelines, World Health Organization, Regional office for Europe, Copenhagen, 1981.
5. Bogdanovic M. Opasnosti od hemijskih akcidenata i postupci za zastitu zivotne sredine, FZNR Univerziteta Nis, 1998.

A CONCEPTUAL FRAMEWORK FOR A DECISION SUPPORT TOOL TO ASSIST IN THE DETERMINATION OF INTRACTABLE OBSOLETE PESTICIDE DISPOSAL OPTIONS

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The assessment of technologies for disposal of obsolete pesticide stockpiles has been, and continues to be, an arduous task. Many present strategies identify the need to consider mutual adaptation of technology and country characteristics. Whilst providing a useful theoretical basis, these strategies offer insufficient support in relation to implementation. Research at ICSER has centred on methods to implement this concept by focusing specifically on the technical aspects of the problem. Combining GIS, database and distributed modelling systems, the author has developed a framework for a decision support tool whereby possible disposal options are identified. Emphasis is placed on the obligations of the Basel and Stockholm Conventions, lifecycle considerations, technological capability and country autonomy. The result will be a tool that synthesises diverse quantitative and qualitative data and provides a solid foundation for further discussion pertaining to obsolete pesticide stockpile amelioration.

Keywords: Obsolete pesticide disposal technology selection, GIS decision support tool, technology assessment.

Introduction

Investigation of intractable hazardous waste disposal options is obligatory for Basel Convention signatories, mandated by the proximity principle. Obsolete Pesticide Stockpiles (OPS) often present a source of intractable waste, since organochlorine components, in particular, are difficult to treat and require sophisticated technologies for environmentally sound disposal (POPs component being mandated by the Stockholm Convention). For countries with no facilities capable of processing these waste streams, comparison between the development of new waste disposal facilities versus export to external agents is onerous. Firstly, the comparison is complex - there are a multitude of factors that must be considered (e.g., applicability, cost, environmental benignity, public acceptability etc...). Secondly, the knowledge required to sufficiently compare options is esoteric and the available information is fragmented or scarce. To assist with disposal comparison, UNEP (2002) suggests the development of a decision support tool. This paper provides a conceptual framework to further develop such a tool.

Problem Orientation

Problem orientation and structuring are crucial to the analysis of disparate alternatives (Belton and Stewart 2001). UNEPs BAT/BEP guidelines provide a useful set of general principles which in this case may be seen as problem orienters (UNEP 2004). Relevant orienters include sustainability, a precautionary approach, the internalization of environmental costs and polluter pays, pollution prevention, integrated pollution prevention and control, the co-benefits of controlling other pollutants, life cycle analysis and management; virtual elimination of POPs, public participation and the proximity principle (UNEP 2004). Put in the context of disposal technology selection, these orienters reflect the desire to evaluate alternatives in terms of intra and inter-generational justice, environmental performance, risk, uncertainty, cost, and to include strategic factors such as incorporating other waste streams and considering capacity building measures, over the whole of the disposal option's existence. To analyse diverse aspects such as these in a holistic manner, a systems perspective must be adopted (Jackson 2003).

Tools for Enhancing Decisions

System analysis techniques explicitly identify structural elements and their relationships, thereby providing a basis for further investigation through analytical techniques (Jackson 2003). Analytical tools may be used to examine specific technical aspects of the problem. For the evaluation of environmental impacts , Life-Cycle Assessment (LCA) has proven to be a powerful tool, utilising the systems concept to identify material and energy flows and their resultant impacts (Azapagic 1999; ISO 2006). Risk assessment can be used to investigate the likelihood and consequences of specific hazardevents and identify vulnerable parts of a disposal cycle (Vose 2000). Life-Cycle Costing can be used to provide a holistic, economic analysis of disposal options (Assefa, Eriksson et al. 2005). These tools, integrated with less analytical methods such as FAO's Country-specific Environmental and Social Assessment (CESA), or UNEP's Environmental Technology Assessment (EnTA) and Environmental Risk Assessment (EnRA), provide a means of evaluating the aspects presented in the previous section.

ICSER Decision Support Tool

Utilising the above tools, ICSER researchers have developed a conceptual framework for a decision support tool that will aid in the process of intractable OPS disposal selection. Figure 1 illustrates a greatly simplified model sufficient to show fundamental flows. As originally proposed by GIFAP (1991) and later by UNEP (2002), candidate disposal options are initially assessed for waste stream applicability and to identify any "fatal flaws". Inventory input may consist solely of intractable OPS or may include other hazardous waste streams (e.g. polychlorinated biphenyls) thereby allowing strategic considerations to be evaluated. This primary screening allows the early exclusion of obviously inapplicable technologies and focuses effort on realistic options.

Subsequent to primary screening, two divergent but intersecting paths are evident - one relates to the inherent characteristics of technologies used for disposal, the other relates to the characteristics within the country of origin. To assess technological adaptation, initially the candidate waste treatment technology process must be simulated to estimate outputs and to approximate resource input requirements. Most technologies have some intrinsic flexibility, therefore the graphic is represented by multiple layers (e.g., additional autoclave reaction chambers, mobile configurations etc.). If the technology is external and extant, an analysis of siting considerations is not necessary, however if the technology is to be developed within the country, it is important to determine whether commissioning is technically possible. Water availability, electricity supply availability and reliability, availability of laboratory facilities, engineered landfills and industrial water treatment facilities are to name but a few of the prerequisites for technology siting (UNEP 2002). Geographic Information Systems are now the standard method for analysis of spatial information (Malczewski 2006). This tool will adopt a GIS interface to layer resource requirements and determine potential applicability. If no potential sites exist to implement a particular technology, there is little point in further consideration and therefore the option should be discounted.

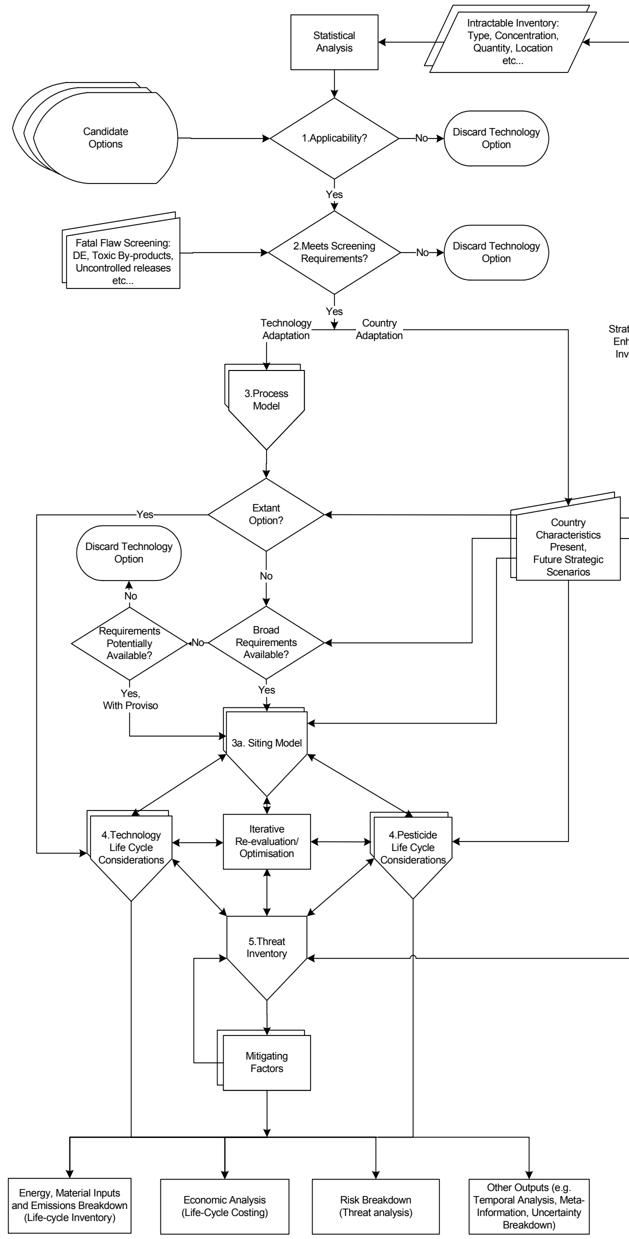

Figure 1: Framework for decision support tool illustrating two life-cycle models, siting model, hazard model and process model, thereby providing outputs shown at the bottom.

If conditions exist to meet potential sitting requirements, the candidate option is considered possible and further site investigation should commence. A preliminary site optimisation tool will be designed to assist in further site investigation. Initially, optimised solutions will be based purely on technical aspects (such as distance to required infrastructure and custom-defined interim storage locations etc.), though users will be able to provide additional detail such as cost factors and legislative considerations. Site investigation is an iterative process; as more information becomes available, optimal location is likely to change. Detailed site investigation should involve extensive stakeholder participation as well as comprehensive social, environmental and economic feasibility analysis hence should be done in conjunction with social assessment tools such as CESA or EnTA.

Following this second phase of screening, life-cycle and risk assessment tools can be used to assist in the identification of system threats and environmental emissions. Through the systematic investigation of each stage of both the pesticide disposal cycle and the technological development cycle, energy, material, and other resource requirements may be calculated. Threats relating to each phase are inventoried and event likelihoods determined. For each hazard identified, mitigation measures can be deduced to reduce the consequences or likelihood of occurrence. Furthermore, temporal factors are included for each phase, allowing an estimation of total pesticide disposal time.

Output from the model will consist of various cost and environmental release estimates, temporal calculations, threats to the smooth functioning of the disposal process, along with uncertainty information. Uncertainty evaluation should be transparent, and should contain meta-data indicating how the uncertainty was derived. By including information about how data were obtained, decision makers may assess the reliability of information for themselves. To compare alternative disposal options, open discussion and consensus, decision tools, or other methods can be utilised.

Discussion

The ability to model disposal processes accurately varies considerably between technologies. For technologies with considerable experience, treatment mechanisms are now fairly well understood and may be modelled with a high degree of confidence (for instance there has been 30 years of empirical testing on high temperature incineration facilities and most releases have been fairly well identified). Novel technologies, on the other hand, possess little empirical large-scale confirmation of performance; treatment mechanisms and releases are less likely to be known. Evaluating the degree of certainty in these situations is difficult, and is best approached through unbiased, expert opinion. Expert collaboration tools (e.g. CyberDELPHI) allow experts to relay perceptions with minimal bias and without fear of repercussion (Vranes, Ghribi et al. 2002). Such methods may be used to generate uncertainty information in this area.

Another process modelling problem relates to the present lack of process disclosure from technology vendors. Commercial sensitivities (e.g. catalysts and other reagents) often prevent the sharing of information on treatment processes, thereby hampering robust analysis. This problem may be overcome through the use of a distributed modelling and web service architecture, hence enabling technology vendors to host process models locally and prevent disclosure of sensitive information (Wallace, Abrahamson et al. 2000). External vetting will still be required however, to ensure reliable information is being disseminated.

Conclusion

Technology selection posits a series of difficult problems for countries wishing to cleanup historical pesticide stockpiles. Research at ICSER has developed a conceptual framework for a decision support tool to provide assistance in the analysis of intractable portions of the waste. The conceptual framework demonstrated in this article is designed to empower decision makers with a means of comparing in-country versus export options for intractable waste disposal. Through it, a tool will be developed to:

- Provide a clear indication of the possible disposal options currently available (externally) and potentially implementable;
- Provide information on environmental releases, costs, and threats over the whole of the disposal process (and beyond);
- Allow countries to insert alternative waste streams and future wastes to plan strategically;
- Encourage more interaction between technology vendors, external disposal providers, and governmental and non-governmental institutions through the development of a web service architecture and vetting system;

- Provide robust assessment of nuanced variables (such as technology development) through the use expert comparison methods;
- Integrate smoothly with other technology assessment tools such as, EnRA, EnTA, and CESA.

Acknowledgements

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References:

1. Assefa G., Eriksson O. et al. (2005). Technology assessment of thermal treatment technologies using ORWARE. Energy Conversion and Management 46(5): 797-819.
2. Azapagic A. (1999). Life cycle assessment and its application to process selection, design and optimisation. Chemical Engineering Journal 73(1): 1-21.
3. Belton V. and Stewart T. J. (2001). Multiple criteria decision analysis : an integrated approach. Boston, Kluwer Academic Publishers.
4. GIFAP (1991). Disposal of Unwanted Pesticide Stocks: Guidance on the Selection of Practical Solutions. Brussels, International Group of National Associations of Manufacturers of Agrochemical Products.
5. ISO (2006). ISO 14040: Environmental Management - Life Cycle Assessment - Principles and framework, International Standards Organization.
6. Jackson M. C. (2003). Systems Thinking : Creative Holism for Managers Hoboken, NJ, John Wiley & Sons, Ltd.
7. Malczewski J. (2006). GIS-based multicriteria decision analysis: a survey of the literature. International Journal of Geographical Information Science 20(7): 703 - 726.
8. UNEP (2002). Destruction and Decontamination Technologies for PCBs and Other POPs Wastes. A Training Manual for Hazardous Waste Project Managers. R. McDowall and J. Vijgen, International Centre for Sustainability Engineering and Research: Auckland, and Secretariat of the Basel Convention (SBC): Geneva, Switzerland.
9. UNEP (2004). Guidelines on best available techniques and provisional guidance on best environmental practices relevant to Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants. Geneva, United Nations Environment Programme.
10. Vose D. (2000). Risk analysis: a quantitative guide. New York Wiley.
11. Vranes S., Ghribi M. et al. (2002). Software Toolset for Sustainable Decisionmaking. British Academy of Management Conference, London.
12. Wallace D.R., Abrahamson S. et al. (2000). Integrated design in a service marketplace. Computer-Aided Design 32(2): 97-107.

DISPOSAL OF PESTICIDE WASTE IN POLAND – CURRENT STATE

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Pesticide waste disposal projects have been ongoing in Poland for the past 11 years. Within this period, about 70% of underground tombs, containing 12000 tons of obsolete pesticides have been closed. Also, pesticide waste stored at warehouses throughout the country has been disposed of regularly. The major issues related to these activities involve:

- *problems with financing and proper tendering procedures,*
- *vague laws regarding land reclamation,*
- *still unknown exact amount of waste to be disposed of.*

Despite some difficulties, the experience gained in recent years allows for efficient progress in terms of disposing of pesticide waste stored in tombs and warehouses by 2010, stemming from Poland's obligations under the Stockholm Convention.

Currently however, the problem of tombs and warehouses is not the biggest threat posed by the pesticidal waste in Poland. The largest site storing waste containing, among others, persistent organic pollutants (POPs) and other pesticidal waste is the "Rudna Góra" Central Waste Landfill at the "Organika-Azot" Chemical Plant in Jaworzno. The landfill stores close to 160 thousand tons of waste, out of which 88 thousand are classified as hazardous. The mix-up of the waste at the landfill as well as the overstocks of waste at the Plant make the site the number one threat in Poland, and possibly in Europe. The location of the site in the Vistula River Basin caused the site to be placed on the list of "hot spots" drafted for the Helsinki Convention on the Protection of the Marine Environment of the Baltic Sea. Large amounts of contaminants being released from the site as well as the site's unfavorable hydrogeological location demand taking immediate and radical steps to stop the spread of contaminants. Considering the enormous scale, it seems necessary to engage the international community to help resolve the problem.

The paper demonstrates the process of closing an underground tomb exemplified by the site in Klotyldzin, in the Wielkopolskie province, remediated at the turn of 2006 and 2007. It considers the obstacles encountered in Poland and explains ways of resolving them. It also describes the situation of the "Rudna Góra" landfill in Jaworzno.

Key words: disposal, pesticide waste, landfill, underground tombs, site reclamation, POP's, obsolete pesticides, tomb liquidation.

Introduction

In Poland, obsolete pesticides have been regarded as a serious ecological problem for over a decade. The problem involves two separate issues: number one (1) is tombs and warehouses; and number two (2) is the "Rudna Góra" post-production waste landfill owned by a chemical plant producing pesticides called "Organika-Azot" S.A. in the town of Jaworzno.

It is estimated that in Poland there were close to 300 tombs containing around 15,000 – 20,000 tons of obsolete pesticides and not all of them have yet been found and inventoried. Currently, after several years of efforts, financed mostly from national funds, there are still around 120 tombs left with 5,000 – 7,000 tons of pesticides. That means that about 70% of waste has already been cleaned up. It is estimated that all tombs should be closed by 2010, but we will still have to deal with contaminated sites, which pose varying degrees of threat to underground water, as it is impossible to fully reclaim sites where contaminants already spread throughout large areas of land surrounding the tombs. As for the Rudna Góra landfill, at this point, there are no prospects for an effective way of eliminating the threats posed by the site [Pruszyński et al. 1996; Stobiecki S. 2003].

Tomb liquidation

Tombs were mostly underground concrete tanks, usually designed as wells made of concrete rings, that oftentimes turned out to be leaking right after they were constructed. The piles of "historic" pesticide waste gathered in these tombs and warehouses contain at least 6 out of the 12 substances that belong to the so called Persistent Organic Pollutants (POPs), which are the subject of the Stockholm Convention regulations addressing the removal of highly hazardous substances from the environment. They are: aldrin, dieldrin, DDT, heptachlor, toxaphen and hexachlorbenzene. Occasionally, we can also find: chlordane, endrin and mirex, also considered as POPs.

The most significant hazard posed by the pesticide waste stored in the tombs, directly in the ground or on the surface is the chance of contaminating surface or ground waters. Contaminants spread slowly, yet they are very dangerous due to their persistence and a lack of effective methods for their disposal. The majority of underground tombs inventoried throughout Poland are found to be leaking various amounts of substances into the adjacent areas. The level of threat they pose depends on the proximity of their location to underground water reservoirs and surface watercourses, and especially on the permeability of the soils surrounding them.

To a lesser degree, some local hazard may also come from the contaminants being spread as a result of a natural disaster (for example a flooded tomb or warehouse, or a warehouse on fire).

Usually, the standard process of closing an underground tomb involves waste excavation, packing it into certified drums and transporting the drums to a hazardous waste incinerator where they undergo thermal neutralization. The concrete structure of the tomb is taken apart, broken and transferred to a hazardous waste landfill, just like the contaminated ground removed during site reclamation [Stobiecki S. et al. 2005].

Projects like that are mostly funded by national and provincial funds for environmental protection and the contractor performing the cleanup is selected in a public bidding process. So far, the EU aid funds have not been used much for this purpose, although they could certainly be helpful. The currently used system of funding the projects is suitable for large, province-wide projects, but it causes problems in the bidding process. Oftentimes, it is impossible to accurately describe the scope of work, which is a statutory requirement, due to incomplete assessment of a site. In most cases, there is incomplete data on the amount of waste stored at the site, and the level of site contamination. The most common issue is the presence of ground pits filled with waste, which are usually in close proximity to a tomb, but remain undiscovered until the site is actually being excavated. Their uncovering affects the scope of work and leads to problems with funding for the projects. There is a risk of matching the scope of work to the amount of funds available, rather than the environmental requirements of the site. Therefore, detailed inspection of a site, including site exposure and environmental testing is crucial. The inventory drafted in 2004, included 29 sites with the “no data available” note, and there were 5 provinces with “missing” tombs, i.e. there were no data on tomb location and amounts of waste. Efforts aiming at locating the tombs should start immediately, or else they will become a potential source of environmental threat for decades to come. Another important issue is to determine the scope of reclamation for sites that are already polluted, with contaminants reaching underground waters. In the case of permeable ground layers, contaminants can spread to such an extent that ground excavation and removal may be impractical for economic reasons. In such cases, it is important to limit any further expansion of contaminants and provide constant monitoring of contaminants natural decomposition in the soil.

Because of some changes being introduced to the act regulating public bidding, there has been a tendency among local community and county governments to invite interested parties for bidding on a smaller scale projects, involving just one or a few tombs. In these cases, it is possible to assess the site more accurately and proceed with the project faster, in compliance with all applicable regulations. The authors of this paper consider this to be the preferred method of dealing with the issue.

Despite the fact that the overall organization of the projects is not perfect, mainly due to a lack of standard guidelines on how to perform site reclamation, imprecise laws and regulations and randomness with regard to site cleanup order and fund allocation, the projects are being completed and we can see that in the future the problem of pesticide waste stored in tombs and warehouses will be resolved, or at least significantly reduced. There is still a chance that the deadline for site cleanup set in the national strategic plans for the year 2010 will be met [Stobiecki T. et al. 2004].

The problem of the “Rudna Góra” Landfill

The situation looks different for the “Rudna Góra” landfill in Jaworzno, which is a real and unsolved problem of transborder ramifications, placed on the list of “hot spots” drafted for the Helsinki Convention on the Protection of the Marine Environment of the Baltic Sea. The landfill, which takes up 20 ha, stores about 160,000 tons of waste, of which 88,000 is hazardous. The different types of waste cannot be separated, because they are all mixed together. Most of them are wastes produced as a result of syntheses of organochlorine insecticides: DDT, lindane, tetradifon and metoxychlorine, but there are also other pesticide active substances, breakdown products and post-synthesis waste. Underground and surface waters in the Vistula River basin flowing into the Baltic Sea are mainly contaminated with linden, inactive HCH isomers, chlorfenvinfos and substances that belong to the POPs (Persistent Organic Pollutants), like aldrin, DDT and HCB. The efforts undertaken by the company involving collection of some of the contaminated surface sewage and directing it to the company's sewage treatment plant are not enough. So far, there is no clear answer to the basic question of how to clean up the landfill. Will it be sufficient and feasible to cover the landfill with impermeable material to cut off precipitation water, or is it necessary to remove and neutralize all of its waste? There is a project under the "Implementation Plan of the Stockholm Convention" to reclaim the landfill site through covering it up with impermeable ground, but it has not been preceded by any reliable assessment as to the effectiveness of the solution [Sadowski M. et al. 2004]. It is crucial to understand that a wrong decision now can lead to much difficulty or even impossibility of retrieving the waste in the future. The scale of the difficulty of the problem with regard to the subject matter as well as funding, compounded by the unclear ownership status of the site make it impossible for us a country to resolve it [Waleczek K. 2006]. It is a case of its own, where the universal rules of the EU law like "the polluter pays", or limitations on availability of public subsidies for companies, imported into the legislation of a post-communist country not only do not help, but rather hinder solving the problem. The Plant, which is the owner of the landfill and is now held legally liable for its cleanup, does not in fact bear responsibility for pollution of the environment, as it used to operate as a state-owned entity under a government, for whom the priority was the size of the production output, not the environmental concern. The current quagmire is a result of the system that vanished into history, the real threat to the environment, however, has remained and the company who operates the landfill is not able to resolve it by itself. The help of the government and maybe even other nations is indispensable in this case. It seems that actions should concentrate around programs and regulations related to the protection of the Baltic Sea, which utilize the research and scientific potential of the Baltic states, who should be interested in finding an effective solution to the problem. Resolving the problem of the Rudna Góra landfill requires a supervisory input and coordination of a number of aspects – legal, organizational, financial and technological. It is crucial to, first of all, conduct a final environmental impact assessment of the landfill (perhaps by a group of international experts) and develop an effective technology of neutralizing the site as well as establish collaboration of Poland with other countries, especially the Baltic Sea states. It should be noted though, that at this point there is no plan for any action of this kind, neither are there any implications to resolve the problem any time soon.

Practical action – a tomb in Klotyldzin

The way of proceeding with tomb cleanup in Poland can be well illustrated by the case of the tomb in Klotyldzin, closed in 2006/07. The tomb consisted of 8 wells made of concrete rings with inside diameter of 3.0 m and the depth of 3.0 to 3.5 m, located on an area of 0.12 ha. The wells were mostly filled up with leftover pesticides used in the 60s and 70s of the previous century. Some waste were dug directly into the ground, in-between the wells. Despite the wells being untight and two wells lacking the bottoms, the contamination of the surroundings was not very high, compared to other similar sites and it did not pose a threat to local underground and surface waters.

The tomb location was marked, fenced and appropriate signs were posted around the area. The site had round-the-clock security and only authorized personnel had access to it. The area next to the wells was covered with protective plastic sheets to prevent contamination of the ground during cleanup. Similar protection was provided for the area where the filled-up drums were being stored and prepared for transport.

The tomb closure included the following stages:

- Open the wells, remove excess ground, secure the site.
- Excavate and remove the waste from the wells, place waste into the special HDPE drums (60 l).
- Label the drums, prepare for transport and transport to hazardous waste incinerator.
- Thermally dispose of the waste and drums in a rotary kiln (no reopening of drums necessary) at the SARPI incineration plant in Dabrowa Gornicza.
- Excavate, break and remove concrete structure of the tomb and transport the debris to a hazardous waste landfill.

– Remove contaminated ground from in-between and under the wells and transport to a hazardous waste landfill.

– Explore the site to uncover all ground pits.

– Protect the excavated area with BENTOMAT impermeable sealant (sodium bentonite with water permeability coefficient k<10^{-11} m/sec.), backfill with clean ground and install a layer of clay to prevent the spread of the remaining contaminants with precipitation water.

– Even out and profile the site to recreate soil layers and reclaim the area through forestation.

The project resulted in excavation and neutralization of over 50 Mg of pesticide waste, 164 Mg of contaminated concrete debris and 158 Mg of contaminated ground. 390 m^3 of clean soil was used to fill up the excavated pit. The total reclaimed area was 0.12 ha.

Conclusions

- 70% of tombs containing 12 th. tons of obsolete pesticides have been disposed.
- There is still around 120 tombs left with 5-7 th. tons of pesticides.
- The major issue is perfect technical level of each step of action of disposal tombs.
- There are important problems with financing and tendering procedures.
- There is a lack of good international guidelines including risk analysis during and after remediation.
- Important issue is still unknown exact amount of waste to be disposed of.
- Landfill „Rudna Góra" is a great real unresolved problem with transborder implications.
- For „Rudna Góra" special coordination and technical assistance is needed for develop an effective technology.
- For „Rudna Góra" – organizational and financial solutions should be created.
- We hope that disposal of obsolete in Poland is not infinite process.

References:

1. Pruszyński S., Ludwiczak J., Stobiecki S. Badania i postęp w działaniach nad rozwiązaniem problemu mogilników w Polsce. Postępy w Ochronie Roślin // Progres in Plant Protection. Vol. 36(1), 306-313. 1996.
2. Stobiecki S. Likwidacja nieprzydatnych środków ochrony roślin – błędy przeszłości oraz propozycje i aktualne możliwości rozwiązania tego problemu w Polsce. Zeszyty Edukacyjne 9/2003, Wydawnictwo IMUZ, 116-131.
3. Stobiecki S., Waleczek K., Stobiecki T., Siłowiecki A., Giza I. Polish experience on site remediation following removal of underground pesticide stocks – legal and feasibility aspects. Environmentally sound management (ESM) practices on cleaning up obsolete stockpiles of pesticides for Central European and EECCA Countries. Proceedings of the 8th International HCH and Pesticides Forum, 26-28 May 2005, Sofia, Bulgaria, 109-114.
4. Stobiecki T., Waleczek K. Prawne i praktyczne aspekty likwidacji odpadów pestycydowych. Postępy w Ochronie Roślin, Progres in Plant Protection, Vol. 44(1), 430-437, 2004.
5. Sadowski ystrybucją i stosowaniem środków ochrony roślin. Instytut Ochrony Roślin, Poznań, 12.12.2006 r.

INIDIRECT THERMAL DESORPTION OF DIOXIN AND PESTICIDE CONTAMINATED SOIL AND BUILDING RUBBLE

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An indirectly heated rotary kiln is being used to treat soil and building rubble contaminated with dioxins, pesticides and raw materials and by-products from pesticide production. The overall project is complex and multi faceted involving not only the treatment but also the decontamination and demolition of the buildings, removal and treatment of old production plant and excavation. The problems encountered in protection of the environment and local population from fugitive emissions, the health and safety aspect of the workers and their monitoring had serious consequences for the project and its cost and are themselves in some respects ground breaking. This paper will concentrate however on the technical and chemical aspects of the thermal treatment and the measures required to mitigate expected and some unexpected complications.

Introduction

Within the boundaries of an operational chemicals complex, north of Prague in the Czech Republic are old production buildings and surrounding ground heavily and very heavily contaminated with chlorinated hydrocarbons, typically HCB and HCH (lindane) from earlier pesticide production and by-product recovery activities. The site gained notoriety due to the high levels of dioxins found both within and outside of the production and research buildings. The fact that the site is directly on the river Elbe which then flows north into Germany and had flooded as recently as 2002 was only one of the negative aspects which pressed the Czech government to implement remediation operations. The dioxins problem had been the reason for immediate shutdown of those particular facilities more than 30 years ago without any decontamination or decommissioning works having taken place.

Piloting and complex permitting with public and NGO participation took up time at the beginning of the project but 10 months after physical work was allowed to start at site the remediation and materials treatment were in full operation. Now, one year after this we are still encountering new aspects which require fast adaptations to maintain operations. Within this current year the contracted works will be completed. Follow up work, treating other contaminated areas within the redundant areas of the complex are in the planning phase.

The UK based company, TCSR, which supplied technology, equipment and project management teamed up with the large French company Suez-Sita to perform the works.

Project Overview

The project encompassed; site detailed assessment, a pilot project to prove the selected technology with local materials, planning and permitting, civil works including containment buildings, supply and erection of all equipment, assembly, decontamination, old equipment removal and demolition of buildings, excavation of soil, processing of all materials with minimum recourse to off-site incineration, back-fill and site restoration.

At the point of maximum activities we had over 150 people working on site. All work in the contaminated areas requires full personal protection clothing and face masks with forced air filters or external air supply. The type of suits required is area specific dependant upon the local concentrations of dioxins in the air. Blood samples are taken regularly from all workers and staff entering contaminated areas and controlled by the medical authorities. All buildings and areas contaminated with dioxins as well as all processing areas are enclosed in a containment building, including the original main five storey processing building. This containment is kept under negative pressure relative to the atmosphere by a large blower system with multiple filters. Process off-gas and exhaust air stacks are extensively monitored and ambient air around the site monitored by 4 external sampling stations.

Original estimates of materials to be treated were;

Soil	25,000 t
Building materials	10,000 t

Steel	3,000 t
Chemical wastes	160 t.

The soil quantities are increasing as we excavate and find areas more contaminated, especially with buried chemicals dumps and we are now required to excavate within the water table as a measure to reduce loading on future ground water treatment.

Processing Plant Description

Processing plant selection was based on the pooled experience of the design and operating team from previous operations of thermal soil treatment and pyrolysis plants and operation of the BCD chemical treatment process. Improvements to the latter were tested in the piloting phase and proven to be effective.

An indirectly heated, gas fired rotary kiln with a nominal capacity of 5-7 tonnes/hour was selected but with slow over dimensioned soil transporting equipment to reduce wear. This has proven to be effective since we have had only minimal repair work on moving parts this far into the project, contrasting with previous experiences where extensive repair was required every few months.

Parallel to the kiln are 2 induction furnaces, sealed and electrically heated to treat steel parts on a batch operation basis.

The combined off-gases are quenched and filtered in a number of processing steps followed by activated carbon filters. A requirement of the authorities was that we add a treatment step to remove volatile organic compounds and carbon monoxide which forms under the pyrolysis conditions within the kiln, although the absolute quantities produced are small. Thermal oxidation was frowned upon and so we installed a catalytic oxidiser.

Cyclone dust, filtered sludge from the quench and dust scrubber, in which the cracked, vaporised or sublimated contaminants are trapped together the more or less pure waste chemicals removed from the old buildings are then treated in the BCD process.

This is a closed batch reactor in which in the presence of a donor oil, catalyst and sodium hydroxide at elevated temperatures the organo-chlorine molecules are cracked to form salt and carbonaceous deposits. At the end of the reaction, which is non selective as regards organo-chlorine compounds the oil is removed and recycled back to the reactor and the solid residue can in most cases be mixed back into the treated soil.

Due to the fact that the processing area requires protective clothing and face masks (PPE) and therefore can only be entered through changing rooms and exited through personnel decontamination locks, access is time consuming. For this reason a comprehensive control and information exchange system was provided for the external control room. In addition an observation monitor linked to the central control system was provided for the field operators.

As well as the main processing plant and the large exhaust air system we were required to add a small dedicated waste water treatment plant as the main waste water plant on-site was unable to handle dioxins or other non-biodegradable pollutants. Since the costs of this small plant are disproportionately high, we are obliged to minimise the amount of waste water generated.

Operations

Because of access problems, initial proving of equipment and controls was performed with non contaminated soil, to avoid PPE and delays in this phase.

One of the measures taken to reduce waste water was a recycling of steam produced in the soil cooler using a spray cooler similar to that used in the main process gas condensation and scrubbing. Typical teething problems occurred with sludge blockages. Piping changes and water jets were added to alleviate this and although the fine dust was abrasive it remained easily in suspension in the main water circuits.

Operation of the kiln, the metal parts furnaces and the BCD reactors proved to be better than expected considering the long start up delays experienced by other waste and soil pyrolysis plants previously. This was partly because of the benign nature of the soil in the opening phase and the fact that we are not trying to couple kiln heating with energy recovery.

The biggest unexpected surprise of this phase was the behaviour of the Catox unit.

Although we had specified the possibility of small amounts of volatile chlorinated Hydrocarbons getting as far as the Catox, this had not been considered in the selection of catalyst and control system of the Catox by the supplier. On research we found that the different mix of pollutants in the soil, principally, HCB, HCH in all its isomeric forms and PCP were cracking in the kiln, where soil exit temperatures are of necessity above 580°C, and producing not only lower chlorinated benzenes, but vinyl chloride, tetra chloromethane and other volatile species which were neither condensed upstream of the Catox, nor retained with sufficient efficiency in the activated carbon filters.

This resulted in partial, reversible poisoning of the catalyst which necessitated much higher operating temperatures.

Volatile Chlorinated Hydrocarbons

Table I

Volatile component	**Concentration, mg/m3**
Vinyl chloride	202.2
1,1-dichloroethylene	5.6
dichloromethane	0.23
Trans-1,2-dichloroethylene	3.5
Cis- 1,2-dichloroethylene	4.0
chloroform	15.9
1,1,1-trichloroethane	2.1
1,2-dichloroethane	1.3
tetrachloromethane	1031
trichloroethylene	5.2
tetrachloroethylene	1.0
chlorobenzene	793

By partial change out of catalyst to one expected to be more resistant to chlorinated species and more so by changing the control logic and addition of an extra air supply nozzle to better regulate temperature within the Catox reactor we were able to maintain TOC emissions below the limit of 10 mg/m3. Since this value also includes methane, we are operating at what we understand to be the limits at which a Catox unit can function.

A practical constraint imposed on the project execution is the lack of space. Both because the contaminated areas extend up to boundaries imposed by other buildings and the cost of the containment there is not sufficient space to store and homogenise large volumes of excavated soil. Hence the processing plants must treat material more or less as excavated. This means big fluctuations in feed composition to the main processing unit, the kiln. Moisture is one factor, which can be controlled by adjustment to feed and kiln temperatures, but more significant and more problematic are the fluctuating, levels of contaminants. For dioxins, there are no processing effects since the overall quantities look serious in the units in which they are measured but are insignificant as far as the processing equipment is concerned.

The other main contaminants, HCB, HCH, PCP are more significant. Initial excavations brought feed with an average of 1,000-5,000 mg/kg, so called OCP's, a sum parameter of the main expected pesticides. However half way through the project values would vary between 20,000 and 90,000 mg/kg. These changes brought with them new operating problems.

Increasing OCP input content produces higher concentrations of volatile chlorinated species, which suppresses further the activity of the Catox catalyst. Obviously this also will produce higher concentrations of HCl in the off-gas.

Dioxins are monitored in our off-gas stack on a weekly basis, in a semi-continuous sampler developed for this project. We must admit that this device polices our activities quiet well and reports any sins to the controlling authorities.

On occasions we exceeded the stipulated limit of 0.1 ng/Nm3, although it should be noted that our process stack volume is about 2000 Nm3/h, so that the environmental impact itself, at all times was minute.

We concluded that dioxins were being created in the Catox, upstream of which are both activated carbon and HEPA filters. Measurements upstream of the Catox confirmed this.

Inlet Feed Compositions

Table 2

date	OCP's mg/kg	TOX mg/kg
05.11.06	4200	
05.16.06	220	
08.07.06	1500	
11.21.06	1800	
11.22.06	2000	
12.02.06	680	
12.12.06	940	
12.13.06	20000	
01.21.07	57000	160000
01.21.07	58000	74000
01.22.07	5600	3600
01.22.07	20000	31000
01.26.07	4200	2000
01.29.07	710	810
01.29.07	40000	140000
01.29.07	53000	150000
01.30.07	45000	150000
01.31.07	2200	1600
02.04.07	9300	4700
02.04.07	2500	2400
02.04.07	18000	24000
02.05.07	19000	28000
02.13.07	69000	26000
02.14.07	72000	20000
02.20.07	70000	
02.21.07	110000	
02.21.07	48000	
02.22.07	15000	
02.28.07	14000	
03.01.07	29000	
03.05.07	6000	
03.07.07	27000	
03.08.07	15000	

Both of these problems; the HCl and the dioxins, were simultaneously solved by the addition downstream of the Catox of a high performance bag filter and the injection upstream of this filter of sodium bicarbonate and activated carbon, pre-mixed. With hindsight this filter should have been in the original design.

Another aspect and problem for operations is the production of gum like deposits along the whole off-gas treatment line up to the Catox, irrespective of the upstream filtration effectiveness. After eliminating other possibilities we concluded that the gums/resins are formed by a continuing polymerisation process of materials such as vinyl chloride. Reducing temperature in the gas treatment line slows this process, but as of writing this paper we are still seeking better solutions. HEPA filters and flame arrestors are blocking with varying frequency.

The third set of effects of such large OCP content in the feed is caused by the sheer mass of such species in the condensing off-gas. It should be noted that there is a 10 fold and more increase in the concentrations in the recovered dust from the vapour stream. This is of course the whole point of the exercise, namely to concentrate the chlorinated organic species in a much smaller stream and then destroy them in the BCD reaction.

However in such concentrations relative to the inert mineral dust, high density, sticky agglomerations are formed which do not stay in suspension as does fine soil dust. This required a different approach to the handling of the quench water circuit and removing these denser agglomerates before they could block heat exchangers and other critical equipment.

As we proceed through the project we are encountering worse feed materials and having to adapt and modify. A waste treatment plant cannot be considered in the same light as a normal production unit. Each day is different.

Despite technical difficulties we have generally maintained production at an average of 2000 tonnes/month and are on schedule to finish this phase of the work by the end of the year.

Interestingly high OCP input into the kiln did not reduce the remediation effectiveness of the kiln. Raising the treatment temperature by as little as 20°C maintained our output levels well below our backfill criteria.

Soil Output Concentrations

Table 3

Date	I-TEQ PCDD/F ng/g	Σ OCP mg/kg
5.11.06	0.0089	4.2
5.12.06	0.0017	0.15
5.25.06	0.0018	<0.1
6.08.06	0.0008	0.11
6.28.06	0.0012	<0.1
7.04.06	0.0012	<0.1
7.19.06	0.0046	0.10
8.06.06	0.0031	0.36
8.28.06	0.00067	0.28
9.01.06	0.0048	0.36
9.14.06	0.0013	0.23
10.14.06	0.017	0.76
10.25.06	0.012	1.6
11.01.06	0.0	0.23
11.22.06	0.028	0.42
12.04.06	0.097	0.9
12.19.06	0.013	1.4
1.07.07	0.00017	1.3
1.21.07	0.028	1.2
2.04.07	0.0034	0.22
2.26.07	0.0082	0.38
3.01.07	0.004	0.79
3.07.07	0.058	0.26

OBSOLETE PESTICIDES IN KAKHETI REGION, GEORGIA

Khatuna AKHALAIA

Milieukontakt International, Georgia

Old stocks of pesticides are threatening public health and the environment in almost every former Soviet country. Most of the time these so called 'obsolete pesticides' are kept in badly maintained hangars. Sometimes the local population has taken the hangars even apart, leaving thus the heavily toxic pesticides in the open air and consequently they are leaking into the underground and ground water.

In the framework of "Elimination of the acute risks of obsolete pesticides in Moldova, Georgia and Kyrgyzstan." Milieukontakt International is implementing a multi-stakeholder pilot project in the Kakheti region of Georgia for safeguarding obsolete pesticides and reduces their actual potential environmental impact.

The situation in Georgia concerning obsolete pesticides is serious. Generally in old storages the roofs have been leaking and pesticides were flooded in water. Pesticides were found in open air and around a large landfill with 2700 tons of pesticides. The guarding fence was completely demolished and the materials have been taken away by local inhabitants that used them as building material.

Policy about Chemical safety in Georgia

TheStockholm convention on Persistent Organic Polluters (POPs), signed in 2001, targets an initial list of 12 highly toxic chemicals that governments are to ban or seek to reduce and eventually eliminate. In April 2006 the Georgian parliament ratified the Stockholm convention.

One can interpret that this is a political willingness to act on the POPs and environment more in general. However there are also indications that the political will is scattered and there is not a strongly developed common approach to environmental issues. The ratification of the Stockholm convention must be regarded as a great achievement since it can help Georgia further in developing new measures to work on POPs.

The UNECE Convention on Access to Information, Public Participation in Decision-making and Access to Justice in Environmental Matters was adopted on 25th June 1998. Georgia has ratified the Aarhus convention as well. This convention is important when working with pesticides since together with requirements in the Stockholm convention it addresses the needs and obligation to inform the public and involve stakeholders in decision-making regarding the activities related to pesticides.

Georgia also signed the Basel convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal.

Georgia does not have a law on waste, including pesticides, and waste management. Currently there is a draft law on waste including hazardous waste. Hazardous is regarded as the responsibility of the MoE.

There is the Law on Transboundary Movement of Hazardous Wastes in Georgia – 1997. All requirement of Basel convention are taken into account in this law.

Activities under the Project in Kakheti Region: First step was to establish an Inventory Working Group (WG). Activities in Kakheti region generally carried out by WG members (8 persons). They are qualified in different fields. Results of Inventory and Risk assessment showed that 5 Priority sites possess 85% of the total risks and that by cleaning up these sites (204 tonnes Obsolete Pesticides) these risks will be eliminated.

After the Inventory and risks assessment Process the WG presented possible Central storages, but most suitable was the building in Village Badiauri. This former building of Meteorological Center belongs to the Ministry of Environmental Protection and Natural Resources in Georgia. The Reconstructed Central storage meets the standards of FAO technical requirements which were prepared by Tauw. The First step of Repackaging training was already done by Berto Collet from Tauw.

During the activities, WG members, periodically organize awareness rising campaigns. Articles in Newspapers, radio announcements and meetings with local population were generally prepared by WG members.

Milieukontakt International has an interesting approach during implementation of the multi stakeholder Project.

The Project Group works very effectively and it is very interesting to find out more and more opportunities for elimination of risks from Obsolete Pesticides, such as within the New European Neighborhood policies. In the frame of the European Neighbourhood Policy Georgia (as other neighbourhood countries) can get more financional support to finally avoid and get rid of obsolete pesticides from the Territory of Georgia. The National Action Plan and the bilateral agreement of each government with the EU is the instrument from each country where Obsolete Pesticides should be mentioned and the activities can be built up adequately.

MIRRORING OBSOLETE PESTICIDES ISSUE OF BANGLADESH THROUGH INTERNATIONAL STANDARDS

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Obsolete pesticides in Bangladesh mostly comprised organochlorine (persistent organic pollutants i.e., POPs), organophosphate and carbamate insecticides. Of them, DDT constitutes the major bulk followed by organophosphates. Pesticides use in Bangladesh was started upon receipt of 3 MT endrin in 1955 and their subsequent application in modern rice cultivation in 1957, which was discontinued in 1960. The use of DDT, BHC, heptachlor, chlordane, aldrin and dieldrin was started after 1960. But DDT, BHC and aldrin were discontinued in agriculture after 1965. The last POP pesticide was heptachlor, which was banned in 1997. Thus there is no formal use of any POP pesticides in Bangladesh after 1997. A total of 691.27 MT of different POP pesticides were procured during 1960 to 1974. A total of 357.105 MT of Heptachlor 40WP, Dieldrin 20EC and Chlordane were imported during 1976 to 1985. A total of 406.18 MT of Heptachlor 40WP and 56.52 MT of Dieldrin 20EC were imported during 1986 to 1997. DDT was the only pesticide produced in Bangladesh during 1966 to 1992. A total of 7706 MT of DDT Technical was produced during this period. A total of 12003.17 MT of 75% DDT were formulated. A total of 500 MT of DDT was imported during 1983/84 under ADB Loan. All these left a total of 524.752 MT of DDT obsolete stocks in different godowns across the country. Besides POPs pesticides, 17 largely used pesticides have been banned so far. A total of 13.65 MT of such obsolete non-POP pesticides have been reported in government stores. However, records of such obsolete pesticides at the companies, distributors and dealers level are not inclusive of the studies. The study did not include environmental risk assessment of the stores, stocks and sites, and their prioritization.

Key Words: Obsolete, organochlorine, organophosphates, carbamates, POPs.

Introduction

Bangladesh, an agrarian country with an area of 1,47,570 sq. km, lies in the north eastern part of South Asia between $20^0 34^I$ and $26^0 38^I$ north latitude and $88^0 01^I$ and $92^0 41^I$ east longitude. It enjoys a subtropical monsoon climate. Temperatures range from a minimum of 7^0 – 13^0 Celsius (45^0F – 55^0F) to 24^0 – 31^0 Celsius (75^0F – 85^0F). The maximum temperature recorded in summer months is 37^0 Celsius (98^0F), although in some places the temperature reaches 40^0 Celsius (105^0F) or more. With 948 persons per sq. km area and 1,495 persons per sq. km of cultivatable land Bangladesh has an estimated 140 million population. Rice is the major crop grown in three seasons almost year-round. Under farmers' field conditions, in certain years and places, crop losses ranging from 35% to 80% – 100% have been recorded for a single insect or disease, especially in the case of rice. Similar estimates apply to wheat, jute, sugarcane, pulses, oilseeds, vegetables and fruits. For examples, estimates of annual loss due to insect pests are 16% for rice, 11% for wheat, 20% for sugarcane, 5% for jute and 25% for pulses (Rahman 2000) and in vegetables 30-40% in general and even 100% losses in case of menace (Rahman 2006). This necessitated the increased use of pesticides in Bangladesh in almost all crops. Moreover, vector-borne diseases particularly malaria was a serious problem in Bangladesh. Malaria is still a serious problem in some areas. This necessitated the use of DDT. But in compliance with the WHO specifications as well as other relevant conventions like Stockholm Convention, Rotterdam Convention, Montreal Protocol Bangladesh banned and/or discontinued the use of most hazardous pesticides, which have left many pesticides obsolete. This article has been prepared to make an account of such obsolete pesticides. The article has been prepared based on the information available from various published articles and reports. Majority of the articles and reports were in connection with the Project BGD/02/G31/IG/99 Bangladesh: Preparation of Persistent Organic Pollutants (POPs) National Implementation Plan under Stockholm Convention (POPs, NIP), Department of Environment (DOE), financed with the grant from the Global Environment Facilities (GEF) through UNDP in compliance to the Stockholm Convention.

Pesticide Registration and Administration Authority in Bangladesh

The Plant Protection Wing (PPW) of the Department of Agricultural Extension (DAE) assisted by a policy body, the Pesticide Technical Advisory Committee (PTAC) is the pesticide registration and administration authority in Bangladesh. The pesticide registration system evolved through four phases such as 1955-73 with Deputy Director (DD), PPW as the single authority requiring no formal procedure, 1973-1980 requiring some trial reports, 1981-1985 requiring approval by a pesticide Standardization Committee and 1985-onward having formal registration system with the Director, PPW of DAE as the registration authority (Rahman 2004).

Trends in pesticide use 1957 to the present

Three tons of endrin received through barter and applied in modern rice cultivation in around 1957/58 land marked the use of pesticides in Bangladesh (former East Pakistan). Government imported pesticides and supplied free of cost until 1974. Subsidy was reduced by 50% in 1974 and totally by 1980. The withdrawal of subsidy initially caused a slight decrease in the consumption. But immediately after a short time, the consumption again started gaining momentum, which is still on the increasing trend (Figure 1a). The pesticide consumption in the country reached 15,160.00 MT of Formulated Product (FP) and 2,443.11 MT of Active Ingredient (AI) in 2000 as against only 3,134 MT of FP in 1977 (Rahman 2000), while it went up to 31,522 MT FP and 9,263 MT A.I. in 2006 (BCPA 2007). A total of 1,153 brands of 173 active ingredients are registered in the country at present (PAQC 2007). The order of dominance of pesticides' groups by use is insecticides>fungicides>herbicides> rodenticides>miticides (Figure 1b). The registration of organochlorine pesticides had either been cancelled or withdrawn by 1997. Thus the order of pesticides by class is carbamates> organophosphates>synthetic pyrethroids>miscellaneous (Figure 1c).

Obsolete pesticides

A significant quantity of pesticides have become obsolete for four reasons such as (i) dumping of imported poor quality pesticides, (ii) poor storage of left-over pesticides, (iii) registration cancellation of certain brands of under-quality pesticides and (iv) banning of certain pesticides.

Figure 1a. Pesticide consumption trend during 1957 to 2006

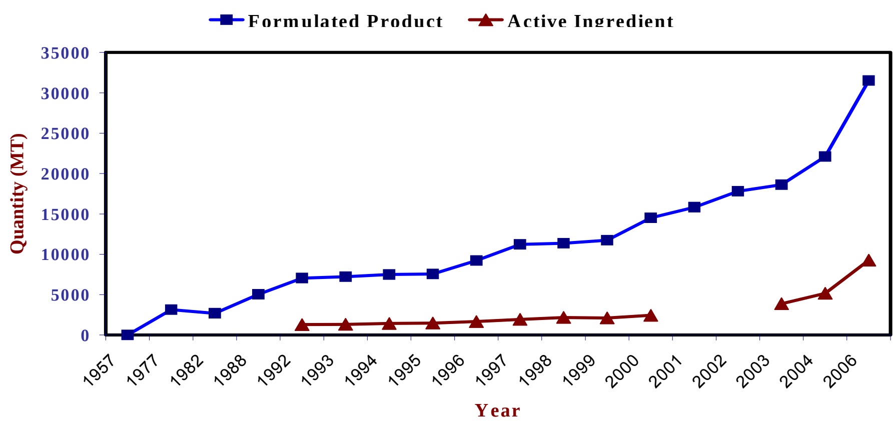
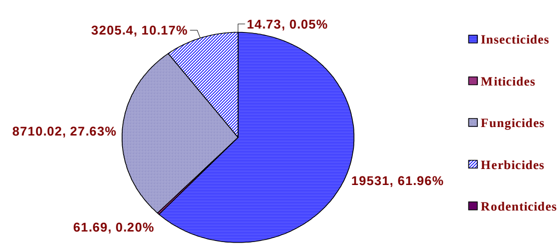


Figure 1b. Market share (MT) of different groups of pesticides in 2006 in Bangladesh



Imports of POPs pesticides

All POPs pesticides used in Bangladesh were imported during 1955- 1997, and afterwards their importation was banned (Rahman 2004, Badruddin 2004). Altogether, there were an estimated 1,452.36 MT-1,533.44 MT of POPs pesticide imported during 1955-1997, of which 713.63 MT were AIs (Rahman 2004, GoB/EADS 2005). These POPs pesticides were imported through supply credit, grant, loan, barter etc., provided by United Nations and donor agencies (e.g., FAO, USAID, the Danish bilateral aid agency, FRG, ADB, etc). Up to 1974, the pesticides procured were centrally housed in Central Stores at Shyambazar and distributed from there to the districts, where they were housed in District Stores and then distributed to *thanas*, and subsequently in *Thana* Stores. From *Thana Stores,* the pesticides were distributed to farmers (Rahman 2004). From 1974 to 1979, imported POP pesticides were similarly distributed via the DAE's network to districts and subsequently to *thanas.* From 1973-1980, private agencies, including foreign manufacturers, became involved in the pesticide import and local formulation business. POPs pesticides imported from 1986 to 1997 were marketed and sold directly by companies through their wholesalers and retailers (GoB/EADS 2005).

he BADC *Official Stock Book* indicated a total of 276.03 MT of Heptachlor 40WP and Dieldrin 20EC were imported during 1974 to 1985. PAB records indicated imports of 357.105 MT Heptachlor 40WP and Dieldrin 20EC during 1976-1985. But all these quantities were either used, buried or destroyed.

DDT import and manufacture

DDT was supplied by the FAO for use in agriculture through 1965. Afterwards, imports for agricultural use were discontinued. DDT used for vector control in Bangladesh was similarly supplied by donors (WHO) up to 1965. Following this, as a plan of its Malaria Eradication Programme, the government constructed a DDT production facility known as the Chittagong Chemical Complex (CCC) at Barabkundu in Sitakundu, Chittagong. The CCC started production in 1966 with a production capacity of 2,000 MT of DDT powder/year. Another chemical complex with the annual production capacity of 4,500 MT of DDT was subsequently established by the private sector near the CCC facility. Both plants were nationalized. Production of DDT by CCC ceased officially on 1 December 1991, but, in practice, was discontinued after 1993. From 1966–1992, the DDT plant/CCC produced a total of 7,706 MT of DDT Technical, and 12,003.17 MT of 75% DDT FP was produced. Out of these, 11,793.27 MT was sold to the Bangladesh Health Directorate for its malaria eradication programme (GoB/EADS 2005). A total of 500 MT of DDT was imported in 1983/84 under an Asian Development Bank (ADB) Loan. However, this amount of DDT was found to be substandard and not accepted by the Directorate of Health Services (DOHS). This DDT was subsequently stored in MSD *godowns* or warehouses in the Chittagong region. A total of 482.904 MT were found in 18,2000 cartoons held in four MSD warehouses, all in poor or obsolete condition (GoB/EADS 2005).

Stockpiles of Obsolete POPs Pesticides

Bangladesh currently has a total of 524.752 MT of obsolete DDT stocks lying in all *godowns* or warehouses, including Plant Protection (PP) stores at the district and *thana* level, DOHS stores and MSD godowns, and stores at the Chittagong DDT plant site (Table 1).

Cumulative stock of obsolete POPs pesticides (DDT) and their present condition

Table 1

Name of POP Pesticides	Quantity in Stock as per Stock Book	Quantity Physically found in Stock	Location	Reasons for Reduction in Stock	Year of Procurement
DDT formulation (local)	5 Kg (.005 MT)	5 Kg (0.005 MT)	PP Store, Chhaga-lnaiya, Feni		Seized from one dealer in 1987
DDT 75WP (Local)	9.81 MT	9.81 MT	District & Upazila Stores of DOHS	Became obsolete over years of stock	1968 to 1992
DDT 75WP (Imported)	500 MT	482.90 MT	4 MSD Godowns, DOHS, Chittagong	Lost, All obsolete	1984
*Microcell/Wassalom DDT Raw Material	32.037 MT	32.037 MT	DDT Plant, BCIC	All obsolete	
Total POP Pesticides (excluding Microcell)	545.9895 MT	524.7752 MT		All obsolete	

Source: GoB/EADS, 2005

Obsolete Non-POP pesticides

As mentioned above, the organophosphates, carbamates and synthetic pyrethroids have replaced the organochlorine pesticides. But because of their high mammalian toxicity, the DDVP, Dichlorvos, Phosphamidon and Monocrotophos have been banned, and the registration of some brands of other organophosphates, carbamates and synthetic pyrethroids have been cancelled, and the lots of some substandard batches of some brands were ordered for withdrawal from the markets. Thus these pesticides might have been stocked at the firm level and undergone obsolete. But their status is not known. However, a total of 13.695 MTs of obsolete non-POP pesticides are lying in different government godowns. These obsolete non-POP pesticides include BPMC, Carbaryl, Cartap, DDVP, Fenitrothin Malathion, MIPC, Zinc Phosphide, Diazinon, Phenthoate, Phosphamidon, Quinalphos, Chlorpyrifos, Copper Oxychloride, Diazinon, Dimethoate and Mancozeb. All of these obsolete pesticides are contained in partially damaged and rusted iron drums, plastic drums, polythene packets, tin containers, plastic containers, bags, bottles, pots etc. These are stored in six divisional government stores. But records of such obsolete pesticides at the companies, distributors and dealers level are not inclusive of the studies. Very limited study has been reported on presence of obsolete pesticides in environmental samples.

Conclusions

The study so far conducted in Bangladesh did not consider the environmental aspects of the stores, production and formulation sites and dealers' stocks. No environmental risk assessment of the stores, stocks and sites have been done. The POPs pesticides management is yet to be undertaken. Moreover, the inventory did not specifically show the stocks at importers, distributor's and dealers levels. The significance and prioritization of the pesticides stocks and stores based on risk assessment may help design the management options of the all the obsolete pesticides including those under NIP.

References:

1. Badruddin M. 2004. Pesticide & Its Management in Bangladesh. In Proceedings of Inception Workshop. Inception Report. Bangladesh: Preparation of the Persistent Organic Pollutants (POPs) National Implementation Plan under the Stockholm Convention (POP NIP), Department of Environment. Paribesh Bhaban, Dhaka, Bangladesh. (www.doe-bd.org/pop/html/publications.htm).
2. BCPA (Bangladesh Crop Protection Association). 2007. Pesticide Consumption Report for 2006. BCPA's Secretariat Office. House # B-142. 1st Floor, Lane # 22, New DOHS, Mohakhali, Dhaka 1206, Bangladesh.
3. GoB/EADS. 2005. Pesticide Inventory of Bangladesh. 2005. Field data collection and preparation of inventories on use/stock/production/sources of POPs Pesticide in Bangladesh. Prepared by EADS (Environment, Agriculture and Development Services Ltd., House 27, 3rd Floor, Road 16 Dhanmondi R/A, Dhaka-1209 Bangladesh) for DoE, MoEF, and GoB. (www.doe-bd.org/pop/html/publications.htm).
4. PAQC (Pesticide Administration and Quality Control). 2007. Plant Protection Wing (PPW), DAE, Khamarbari, Khamarbari Sarak, Farmgate, Dhaka 1215, Bangladesh.
5. Rahman M.M. 2006. Vegetable IPM in Bangladesh, In E. B. Radcliffe and W. D. Hutchison [eds.], Radcliffe's IPM World Textbook, URL: http://www.ipmworld.umn.edu/chapters/rahman. htm., University of Minnesota, St. Paul, MN.
6. Rahman M.M. 2004. Uses of persistent organic pollutants (POPs) in Bangladesh. In *Proceedings of Inception Workshop*. Inception Report. Bangladesh: Preparation of the Persistent Organic Pollutants (POPs) National Implementation Plan under the Stockholm Convention (POP NIP), Department of Environment. Paribesh Bhaban, Dhaka, Bangladesh. (www.doe-bd.org/pop/html/publications.htm)
7. Rahman M.M. 2000. Pesticides: Their uses and Problems in Context of Bangladesh. Paper presented at the National Workshop on Conventional and Nuclear Technique for Pesticide Residue Studies in Food and Environment held on 15-19 October 2000 at IFRB, AERE, Savar, Bangladesh.

THE USE OF UP-DATED POLYETHYLENE PACKAGING FOR TRANSPORTATION AND STORAGEOF HAZARDOUS CHEMICAL SUBSTANCES

Gjusjal' HUSNULLINA

ZTI Company, Russia

Technological progress and population upsurge on Earth led to increase in output of different materials and synthetics, containing chemical compounds, which are hazard to health and the environment. With the advent of numerous chemical enterprises dealing with manufacture and sale of hazardous substances, correct storage and transportation of products in reliable packaging conforming to international standards are of great importance.

ZAO (JSC) «ZTI», leading producer of high quality, cost effective and environmentally safe industrial packaging, is a dynamically developing company.

Since 2004 our company has been the only licensee in Russia and CIS countries of Mauser-Werke GmbH & Co. KG Holding (Germany). Due to this cooperation we have access to the latest global developments in the field of plastic packaging production.

We are ready to offer our customers high quality euro packaging that is approved for transportation and storage of pesticides.

The only criterion of packaging reliability in the whole world is UN Certificate. Our Euro containers are certified according to GOST 26 319 «Dangerous Goods. Packaging» and international regulations for transportation of dangerous goods (packaging group I, II and III) by any mode of transport (UN-approval).

Products, manufactured on state-of-the-art European equipment, are made of high quality chemical resistant raw materials, noted for their good combination of strength and elastic properties, owning to it you can use our packaging within a wide temperature range and be sure for environment safety during transportation of dangerous filling goods.

The product mix includes:

1) Stackable and Palletized Euro Jerrycans 11 L, 21.5 L, 31.5 L, 63 L

Their free-standing design allows stacking without additional packing material. Protruded figured element of the top fully coincides with locating dimple at the bottom of jerrycan.

Your Benefit:

- Euro neck for fast filling and easy discharge
- reliable fixed seal cap ensures protection from unauthorized access to filling goods
- easy manual handling gripper
- even wall thickness distribution allows good stand and stacking abilities
- leak-proof
- chemical resistant

2) Open Top Drum 48 L, 65 L, 127 L, 227-23O* L

For any liquid, solid, loose and paste-like filling goods

Since 1975 this MAUSER development considered to be the standard among plastic packaging all over the world. The products developed by MAUSER are produced by 118 Companies in 48 countries. The Open Top Drums meet the European CEN-standard and are suitable for transportation of liquid, loose, paste-like and solid chemical, petrochemical and food products, including dangerous goods. Its seamless body has no weak points due to it the drum can withstand significant mechanical stress.

Euro drums are completed with removable lids, seal rings, clamping rings of galvanized steel, security pins. 48 L and 65 L drums are completed with hinged handles. It can have pressure relief valve which allows hot product filling and helps to avoid drum deformation due to vacuum forming inside.

Technical Data

Type/Volume (L)	Height/mm	Outer Diameter/mm	Diameter of filling neck/mm	Approval/UN
D-48	490	400	320	1H2/X75/S/05
D-65	630	400	320	1H2/X101/S/05
D-127	798	492	392	1H2/Y174/S/05
D-227/230*	978	585	480	X350/S

*brimful capacity - 230 L

3) MAUSER L-RING PLUS DRUMS 227/232 L* (under license)

For all Liquid Filling Goods.

The L-Ring Plus Drums meet the European CEN-standard and are suitable for transportation of liquid chemical, petrochemical and food products. Due to patent L-Ring area the drum can be transferred by all standard gripping devices. As drum is blown in one operation step its seamless body have no weak points. It can have pressure relief valve.

Technical Data

Type	Weight/kg	Nominal volume/L	Outer diameter/mm	Height/mm	Approval/UN
L-Ring Plus Drums	7.2 standard	232	581	935	Y 1.5/100
	8.5 increased strength				X 1.2/250 Y 1. 9/250

* brimful capacity - 232 L

If you use PE packaging produced by ZAO «ZTI», you will have the following benefits:

• free from corrosion and mechanical damages;
• no deformation during transportation, storage and stacking;
• good stand and stacking ability up to 3 layers high;
• leak-proof;
• good combination of strength and elasticity;
• wide temperature range of use;
• enlarged capacity allows to minimize costs for transportation;
• UN-approved, GOST 26 319 "Dangerous Goods. Packaging";
• easy handling with standard drum lifters;
• smooth surface allows good quality of labeling and marking;
• easy cleaning, multi-trip use;
• low weight;

The main criterion at storage and dumping of obsolete pesticides is the decomposition period of PE. Unlike packaging of another type the period of PE decomposition is 250-300 years. This fact testifies that PE packaging is reliable and safe.

Together, with our customers, we share the responsibility for safe transportation of goods.

Our partners are major chemical enterprises in Russia and CIS which ship the products by all means of transport at long distance.

Eurodrum produced by ZTI Company are used for pesticides repackaging within the framework of POPs disposal projects in Russia and CIS.

Our Euro containers are included in TU on Federal special-purpose program «Elimination of chemical weapons».

ZTI Company guarantees packaging reliability, supply stability and confidence in the future.

All in all it is important to note that the problem of restriction and POPs elimination can't be solved not only by any one country but even by means of regional arrangements.

The ubiquities POPs destruction is one of the main problems of world community. ZTI Company is ready to render direct assistance in solving this problem.

PACK AND TRANSPORT REVISITED, A DESCRIPTION OF ORION'S PCB REMOVAL PHILOSOPHY FROM START TO FINISH

Dirk Jan HOOGENDOORN

Orion b.v., Drachten, the Netherlands

About Orion

Orion B.V. is an internationally operating company specialised in the treatment and handling of Poly-Chlorinated Biphenyl's (PCB's).

Orion's mission is to be recognised as a reliable partner in safeguarding the environment by safe and cost-effective removal and destruction of PCB containing equipment.

Our procedures foresee in packing the PCB-waste on location and sending it in containers to the Netherlands for destruction in our treatment facility in Drachten.

Of course Orion is not unique in providing this kind of service, but as a dedicated and specialized company we have (a need for) an unique and different philosophy.

Our philosophy is to transfer know-how and expertise to local partners aiming to enable each country to have a company trained in the handling of PCB waste. In our experience the advantages are:

- "In country" competence to handle PCB waste and PCB calamities;
- Trust, understanding and good communications between the local company, the environmental authorities, the owners of the PCB waste and Orion;
- Much employment and revenues remain in the local economy;
- Local temporary storage is created, so PCB waste disposal is also available to owners with small PCB waste amounts;
- Quick and adequate response in case of an accident.

Finding a local partner

Orion looks for partnership with existing local companies in the area of hazardous waste collection. This way we use the local expertise in a country and we try to avoid disturbing the local market with competition.

When Orion start to study a new country we introduce the company to the local government (Competent Authorities) and ask them for a list of suitable and licensed organizations for the collection, storage and transport of PCB containing waste. Most of the time the Dutch government is able to support Orion during this introduction.

The next step is to ask PCB-waste owners like the local power companies and the industry for recommendations of PCB-waste collectors. By matching these lists we aim to find a licensed and service oriented partner in each country outside the Netherlands.

The type of company that we usually form a partnership with are industrial & hazardous waste collectors or transformer-service companies.

Cooperation between Orion and her partners

The local partner is supported by Orion when needed. Mostly this will be in the field of marketing, technical support and logistic services. During the first projects Orion can send a specialist to assist to local partner. Most of the support is done by e-mail and telephone. When the local partner has sufficient know how Orion is satisfied and will no longer send technical specialists to assist during the projects.

This period of extra support normally last 1 to 3 years. This depends on the level of existing experience at the local partner and the speed of the market development.

It sometimes occurs that personnel from the local partners comes to train at Orion's facility.

Export documents

TFS documents

Orion opens Trans Frontier Shipment (TFS) Documents for a country for one year from our local partner to Orion. The procedures for obtaining these documents are very familiar to Orion and our requests have been rewarded by all the different competent authorities up till now.

Duly Motivated Request

To obtain the TFS documents for a project, the competent authorities have to give their written statement in which they allow export of PCB-waste to the Netherlands, because there is no capacity for destruction of PCB-waste in their own country. To obtain this statement the assistance of the local partner is very welcome.

Example from Bulgaria

In 2004, to prepare for the enlargement of the EU the Dutch trade minister has visited all the potential new country-members of the EU, so also Bulgaria.

During this visit, Orion, among other Dutch exporting companies, joined the minister. In this week we were introduced to the Bulgarian ministry for environment. The ministry has introduced us to Balbok. After two more visits to Bulgaria, Orion has signed the contract for partnership with Balbok in 2005 and the first PCB-project is finished in 2006.

Balbok is specialized in hazardous waste in Bulgaria. For PCB-waste they did not have a partner with the recycling options Orion could offer.

During the last 3 years Orion and Balbok developed a very nice cooperation. Exchange of logistic and technical knowledge, both ways is working out very nicely. Orion has assisted Balbok during the first project with a sales visit at the client and supervision of the first PCB-project at the clients factory.

Balbok has assisted Orion in obtaining the TFS documents and the transport permits.

Balbok works according to the high international standards for the handling, treatment and storage of hazardous waste. Because of their impeccable reputation, the PCB-project run very smooth and the confidence of the clients and the authorities is very high. This partnership helps to strengthen the reputation and the services of both partners.

Both companies are very enthusiastic about this partnership and both the economy and the environment of Bulgaria and The Netherlands benefit from this cooperation.

SERVICES FOR HAZARDOUS WASTE MANAGEMENT AT VALOREC SERVICES AG

Karine J. SCHNYDER

Valorec Services AG, Basle, Switzerland

Valorec Services AG operates two high-temperature incinerators for used solvents and a high-temperature rotary kiln providing environmentally sound disposal of hazardous waste. The different technologies used allow the treatment of solid, liquid, pasty or gaseous waste. Our incineration plants comply with local regulations. Inspections of our emissions (cleaned flue gas, waste water and solid residues) are performed at regular intervals by the local authorities issuing the licence for plant operation. In the fulfilment of our duties towards the public and the environment we are well accepted and respected even though we operate on the periphery of the city of Basle.

Valorec Services AG is mainly active on the Swiss market. Its major clients for the disposal of hazardous waste range from global multi-site companies like Novartis, Roche, Ciba SC, Huntsman or Syngenta to smaller companies and large-scale hazardous waste collectors. Valorec Services AG offers the largest capacity for the incineration of hazardous waste in Switzerland. Based on the vast know-how gathered by many years of collaboration with leading chemical companies, Valorec Services AG can offer specific solutions and is a well appreciated business partner. Moreover, Valorec Services AG maintains international business relations in Europe as well as overseas. Projects in collaboration with the Swiss Government for the import and disposal of obsolete pesticides from Madagascar, Bhutan and Macedonia have been carried out over the past few years. PCB-contaminated equipment, materials and oils have also been successfully imported from former Yugoslavia, Mexico, and France.

Since 2001 Valorec Services AG has been an affiliated company of Veolia Environment, the world leader in environmental services with headquarters in Paris. With more than 270,000 employees the company has operations all around the world and provides solutions tailored to meet the needs of municipal and industrial customers in four complementary segments: water management and passenger transportation.

Key-words:
- Environmental services / waste management, energy management and solvent recycling.
- Hazardous/special waste treatment for solid, liquid, pasty and gaseous waste.
- Environmentally sound incineration of hazardous waste.
- High-temperature rotary kiln / Static high-temperature incineration plant for used solvents.
- ADR regulation / Swiss authorities / Basle Convention.
- High safety standards, transparency and traceability.
- International Projects / Obsolete pesticides and PCB-contaminated hazardous waste, etc.

Valorec Services AG has its origin in a long tradition of the Basle chemical industry. With companies like Geigy (founded in 1758), Ciba (established in 1884) and Sandoz (formed in 1896) providing the backbone to the development of the Swiss chemical sector, we can look back on a long history. During the second half of the twentieth century, the know-how in this industry gradually developed to a point in 1996 when Ciba-Geigy and Sandoz merged to form Novartis, one of the world's leading pharmaceutical company.

Between 1996 and 2001 Novartis was divided into the three divisions of Novartis Pharma, Novartis Services and Novartis Crop Protection, the last of which later merged with Astra Zeneca in 1999 and to become Syngenta, another market leader in the agro business. The Novartis Services division was made up in particular of five departments, namely "Repair & Maintenance", "Building Services Engineering", "Waste Management", "Energy" and the "Recycling & Solvent Center". As an internal service of Novartis the name Valorec was already known as provider of Waste- and Energy management, including the recycling of solvents. As it focused on its core business, Novartis awarded Veolia Environnement a contract which covers the outsourcing of the environmental services of Waste Management, Energy and the Recycling & Solvent Center at the four multi-customer sites in Basle, Switzerland, on 30th November, 2000. All the outsourced services have been managed since 1st January 2001 by Valorec Services AG, a special purpose company. Along with this spin-off, 320 employees were transferred from Novartis to Valorec. This contract is regarded as the world's biggest contract for industrial outsourcing services.

Veolia Environnement, the parent company of Valorec, is a world leader in environmental services and the only key player providing all environmental services. Located in 115 countries over the world, Veolia Environnement had a turnover of over 25 billion euros in 2005 with a total of over 271,000 employees. Veolia Environnement consists of four different divisions: "Water Management", "Environmental Services", "Energy Management" and "Transportation". Since Valorec Services operates equally in the fields of Environmental Services and Energy, Valorec is organized within the Industrial Markets division of the Veolia Environnement family.

Located in the centre of Western Europe in Basle, Valorec Services AG operates in close proximity to its partners Novartis, Ciba Speciality Chemicals and Syngenta on four industrial sites named Klybeck, St. Johann, Rosental and Schweizerhalle. On all four sites we provide our waste management and/or energy management services to our partners and at the same time to 3rd party clients from the Swiss and international markets. Our range of solvent recycling and waste management services includes the incineration of solid, liquid, pasty and gaseous waste, the incineration of solvents and special liquid waste such as the distillation of used solvents. On the other hand we offer global energy services, which means specifically audits and diagnostics, operation and maintenance of installations, energy and utilities supply, contracting, facility management and, last but not least, outsourcing. Since the outsourcing of Valorec Services AG seven years ago, the number of employees has remained the same at about 320. Valorec Services AG serves 3 partners on site and several hundred customers from the Swiss market as well as a couple of international customers.

Valorec's environmental services and capacity

Table 1

Waste management and solvent recycling	Water and utilities global management
Solvent recycling: • 20,000 t/year • 20 distillation columns • 190 tanks (8,000 m^3) • Supply of new and distilled products • Adapted logistics Incineration of solvents and liquid special waste: • 53,000 t/year • 2 ovens • Combined heat cycle Solid, liquid, pasty and gaseous special waste incineration • 25,000 t/year • 1 rotary kiln • Steam production • Electricity production Industrial waste • Collect, segregation, recycling and treatment	On the 4 sites Valorec Services AG provides production and distribution of utilities and water. • Electricity (340 GWh/year) • Steam (1 million t/year) • Hot water • Cooling water (20,000 t/year) • Compressed air (110 million m^3/year) • Drinking water (2 million m^3/year) • Industrial water (38 million m^3/year) • Deionized water • Waste water management

With regard to the incineration of hazardous waste, Valorec Services AG operates three incineration plants. The regional high-temperature rotary kiln (RSMVA) in Basle for solid, liquid, pasty and gaseous hazardous waste with an annual capacity of 25,000 tons and two further static hazardous waste incinerators for the disposal of spent solvents and off-gas containing VOC at Schweizerhalle which achieve an annual yearly capacity of 53,000 tons. However, it has to be said that the two static hazardous waste incinerators are leased from Novartis, in contrast to the rotary kiln, which is fully owned by Veolia Environnement.

Receiving hazardous waste from our clients means that it has been classified and the ADR regulations are applicable. According to ADR regulations, hazardous waste can be classified as packed for safe transportation. The high-temperature rotary kiln was launched in 1996 with the aim of treating all kinds of organic hazardous waste generated by the chemical industry. Valorec Services is therefore highly specialised in hazardous waste incineration and can show broad experience in all danger classes, whether the waste concerned is an explosive substance, a toxic gas, an organic peroxide, infectious substances or radioactive material, to name just a few. However, although we employ state-of-the-art technology, we should not forget to include alternative recycling solutions in order to create added value. In general it is therefore essential to avoid hazardous waste as far as possible.

With regard to the declaration of hazardous waste in general, the waste producer or the Environmental Health and Safety (EHS) department of a production company will produce analytical data of its hazardous waste and generate a Material Safety Data Sheet (MSDS), as well as safety guidelines for the protection of its employees while handling the hazardous waste. This information will often be entered in a Waste Declaration Card, which the client provides us with when asking for a treatment assessment.

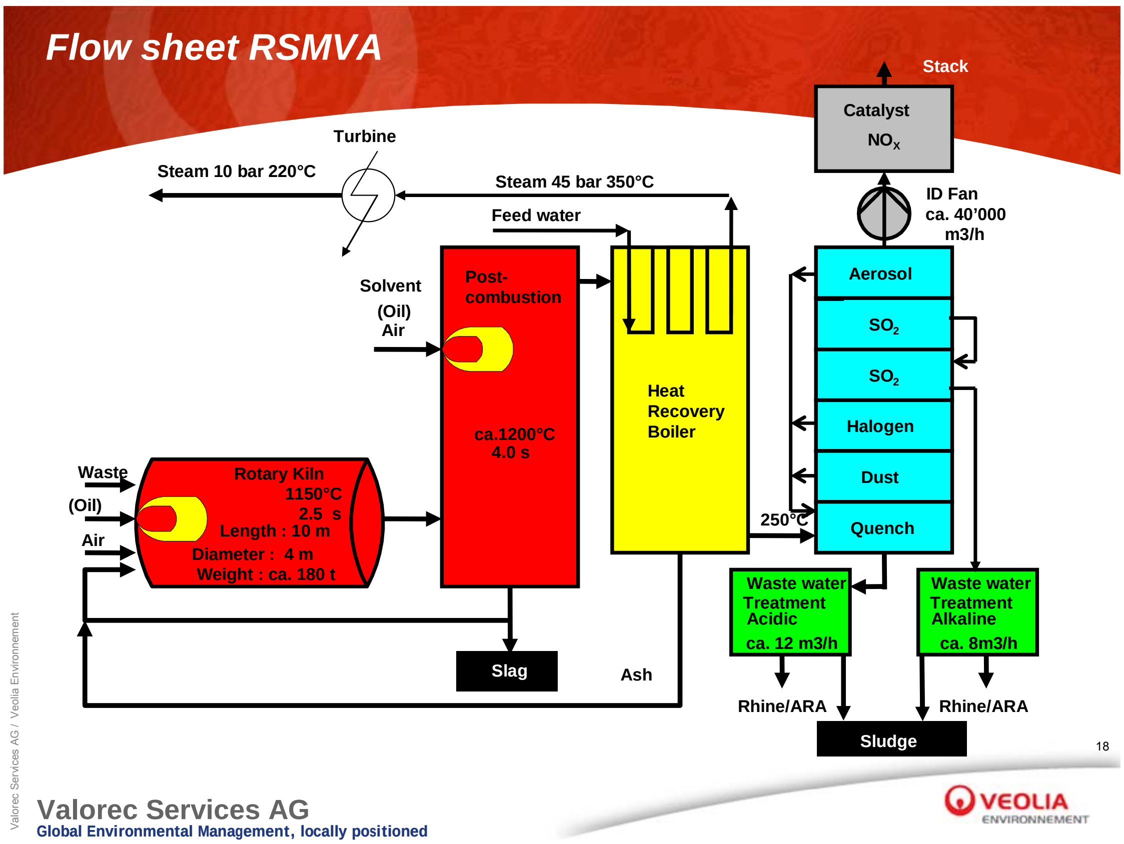
The conditioning of hazardous waste plays an important role for safe transportation and handling of hazardous waste, while also reducing emissions. This is another very important part of the having such an incineration plant located on the periphery of a city. For solid hazardous waste Valorec Services accepts UN approved metal, plastic or fibre drums with a size of up to 200 litres, as well as UN approved cardboard boxes (general dimensions: height = max. 90 cm, diameter = max. 60 cm). For liquid hazardous waste we accept deliveries of 200 litre drums, intermediate bulk containers (IBC) of 1 m^3, Isotanks of 20 m^3 and even deliveries by tank wagons. We are proud of our flexibility and our ability to accept deliveries both by truck and by train directly to our goods receipt department. However, it is important to evaluate the best conditioning processes according to the needs of the relevant hazardous waste, its environmental safety precautions and the technical circumstances of our incineration plant.

Categories of treated hazardous waste in the high-temperature rotary kiln

Table 2

Solid hazardous waste (> 5,700 t/year)	• Filtration residues (aqueous, organic) • Distillation residues • Obsolete raw materials • Expired medicines • Laboratory waste (chemicals, equipment) • Pesticides • PCB contaminated capacitors and solids
Liquid hazardous waste (> 17,000 t/year)	• Spent solvents, halogenated and non-halogenated • Mother liquor from chemical production • Concentrated acids contaminated with organics • Obsolete raw materials • PCB contaminated oils • Active substances from pharmaceutical and crop protection industries
Pasty hazardous waste (> 1,500 t/year)	• Paint residues • Organic slurry
Gaseous hazardous waste (> 700 t/year)	• Freon and halon gases • Liquefied hydrocarbons (butene) • Gases in pressurized bottles

The rotary kiln consists of a specially manufactured oven 10 m in length and 4 m in diameter. The feeding of hazardous waste varies according to the consistency and packaging of the hazardous waste. We have manual handling and semi automatic handling of solid waste, three lances for liquid and one lance each for pasty and gaseous waste. In addition we have burners operating with good quality solvent (as combustible substitute) in the kiln and in the post-combustion chamber. The working temperature in the kiln is of approximately 1150 °C. The residence time of the flue gas is 2.5 seconds. The combustion is completed in the post-combustion chamber, where the flue gas remains at a temperature between 1100 °C and 1200 °C for 4 seconds. While passing the heat recovery boiler the gases are cooled down to 250 °C before entering the flue gas cleaning system, consisting of 2 scrubbers and a SCR reactor. In the next 6 stages the gas is first cooled down to saturation temperature. Then particulate, halogens and sulphur are removed. High removal efficiency is achieved using packing column and Venturi-effect stages for particulate and aerosols. Final treatment of the flue gas includes the selective catalytic reduction of NOx after injection of ammonia. The capacity of this incineration plant for treating environmentally sound hazardous waste of all kinds of aggregates is about 25,000 tons per year.



Picture 1: Flow chart of Valorec's high-temperature rotary kiln

The liquid effluents (treated wastewater), the gaseous emissions (treated flue gas) and the solid residues (slag and metal hydroxide sludge) are monitored. The monitoring frequency of each stream follows regulatory requirements. Waste water is continuously monitored for the following parameters: pH, temperature, TOC and turbidity. Furthermore, a monthly analysis of mercury and salts (sulphate, fluoride, chloride, bromide and EOX) and a quarterly analysis of heavy metals are performed. The waste water from the flue gas cleaning is released in the river Rhine after physical-chemical treatment and the tests that are carried out. With regard to the treated flue gas we undertake continuous emissions monitoring (CEM) in the stack for CO, NOx, FIDC, NH_3, HCl, dust and SO_2. According to the local regulation, the following values have to be met: dust < 10 mg/Nm^3, hydrochloric acid < 20 mg/Nm^3, NOx < 80 mg/Nm^3, CO < 50mg/Nm^3, VOC < 20 mg/Nm^3, dioxin and furan < 0.1 ng/Nm^3. In addition, measurement campaigns, including discontinuous measurements of compounds measured on-line and measurements of heavy metals, fluoride (HF, HBr), dioxins and furans, are performed every three years by an external institute. The slag which is collected after the rotary kiln is evaluated every three months by leaching tests (24 h CO_2 eluate and 48 h CO_2 eluate). We dispose of approximately 2,000 to 2,500 tons per year in a nearby landfill in Switzerland. The metal hydroxide sludge is exported to an old salt mine in Germany, and samples are therefore collected as reference. Valorec

Services AG sent almost 2,000 tons of metal hydroxide sludge for final disposal last year.

The valuable by-products produced are approximately 140,000 tons of superheated steam while incinerating hazardous waste and 5,500 MWh of electricity while operating a steam turbine which expands steam of 45 bar and 350 °C to steam of 10 bar and 220°C. The steam is injected into the grid and distributed to the production buildings of our partners on site; the electricity produced is for our own use.

With our services we fulfil our duties towards the public and the environment not only in Switzerland but also worldwide, as our international project references demonstrate. We have incinerated obsolete pesticides from countries such as Bhutan (43 t), Macedonia (35 t), Madagascar (94 t) and Uganda (38 t). With regard to the elimination of PCB-contaminated capacitors, different kinds of PCB-contaminated solids and PCB-contaminated oils, we have been active in Croatia (75 t), France (12 t), Germany (600 t), Mexico (15 t) and Serbia (70 t). In almost all these projects our services included site assessment, segregation and consulting, especially with regard to packaging, re-packaging on-site according to Valorec's directives and supervision by Valorec's own chemists, and transport as well as subsequent incineration in our plant. According to the size and complexity of the project we have also worked on-site with third parties. Valorec Services AG is used to handling chemical waste on a daily basis and hence has the necessary skill to assess and treat difficult waste, i.e. AIBN (13 t) a temperature-sensitive hazardous waste which we successfully imported from Israel for incineration in our rotary kiln. For this special project, risk assessment, product characterisation and special refrigerated shipment were also part of our service. However, all projects completed abroad by Valorec Services AG were carried out according to the rules of the Basel Convention, ADR regulations and the specifications of our quotations.

In conclusion, we would like to point out that the operation of hazardous waste incineration plants in urban areas is possible and can be well accepted by the public and the environment. However, the commitment of manufacturers and waste disposers like Valorec Services AG is essential for efficient waste disposal. Furthermore safe handling is possible with appropriate conditioning and declaration of the waste and we believe that high temperature incineration is the technology of choice for special waste disposal.

References:

1. Annual report of RSMVA 2007 (Valorec Serivces AG internal document).

A TOXIC-FREE FUTURE: ALTERNATIVE NON-INCINERATION WASTE MANAGEMENT TECHNOLOGIES

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Database of alternative non-incineration waste management technologies in the Russian language is developed. It incorporates technologies for neutralisation and utilisation of production and consumption waste, including obsolete pesticides, technologies for elimination of persistent organic pollutants (POPs), as well as methods of disinfection, elimination and treatment of medical waste. The database allows interested producers and consumers to get information on tested industrial-scale technologies; technologies approaching the stage of industrial application; promising laboratory-scale tested technologies with good chances of further development, as well as on underdeveloped technologies with unclear capacity, that are likely to reach an industrial application scale in the case of further research. In addition to brief description of technological processes, the database contains information on relevant economic considerations, waste treatment costs, health and environmental safety data, contact information of developers and equipment suppliers. Importance of the database is associated with the fact that it contains information about the most appropriate waste treatment and elimination technologies for East Europe, Caucasus and Central Asia (EECCA) region from the whole array of available technologies (the technologies were selected at the base of their economic and environmental efficiency). The database is a unique collection of information materials on experiences of different countries and organisation in the sphere of safe waste management. For the first time, the database allowed a broad range of readers to get access to information on some technologies that were developed in the EECCA countries. Database can be downloaded from the following website: http://www.noburntech.info.

Key-words: toxic, non-incineration, waste management, POPs, database

In the article a database of alternative non-incineration waste management technologies is presented. The database incorporates technologies for neutralisation and utilisation of production and consumption waste, technologies for elimination of persistent organic pollutants (POPs), as well as methods of disinfection, elimination and treatment of medical waste.

Such a database in the Russian language is being developed for the first time. The database developers have managed to collect information on more than 70 modern waste management technologies. The database information would allow interested producers and consumers to get information on all tested industrial-scale technologies; technologies approaching the stage of industrial application; promising laboratory-scale tested technologies with good chances of further development, as well as on underdeveloped technologies with unclear capacity, that are likely to reach an industrial application scale in the case of further research.

In addition to brief description of technological processes, the database contains information on relevant economic considerations, waste treatment costs, health and environmental safety data, contact information of developers and equipment suppliers.

Technologies for incorporation into the database were selected at the base of the following key criteria:

Health and environmental safety of technological processes.

The level of destruction of hazardous components.

Waste treatment costs.

Skilled experts from Russia, Ukraine and Belarus provided their comments on specific technologies and formulated their common position on the database of alternative non-incineration waste management technologies, assessed its importance for addressing problems of adequate and safe waste management; for training of environmental specialists; for public awareness raising and for professional support of decision-making in the sphere of environment.

Besides that, importance of the database of alternative non-incineration waste management technologies is associated with the fact that its developers sought to select the most appropriate waste treatment and elimination technologies for East Europe, Caucasus and Central Asia (EECCA) region from the whole array of available technologies (the technologies were selected at the base of their economic and environmental efficiency).

Information on alternative non-incineration waste management technologies was collected from different sources, including information materials of the Global Environmental Facility, the World Bank, UNEP, US EPA, as well as publications of theoretical conferences and specialised seminars. Besides that, information on technologies was provided by R&D institutes and laboratories operating in the sphere of waste treatment, as well as by NGOs.

Therefore, the database is a unique collection of information materials on experiences of different countries and organisation in the sphere of safe waste management. For the first time, the database allowed a broad range of readers to get access to information in some technologies that were developed in EECCA countries.

Now, EECCA countries actively fulfil their commitments under international environmental conventions. Some of these conventions are of direct relevance to waste treatment and elimination issues, namely the Stockholm Convention on POPs and the Basel Convention on Control of Transboundary Movements of Hazardous Wastes and their Disposal. Besides that, EECCA countries actively participate in implementation of the Strategic Approach to International Chemical Management (SAICM), approved in February 2006 by the International Conference on Chemical Management. The Global Action Plan of specific activities for SAICM implementation incorporates a special section on waste management matters. It is clear, that the above international conventions (as well as some others) would require EECCA countries to apply an adequate approach to addressing waste management problems.

The proposed database would allow representatives of different social sectors - from governmental authorities, industrial facilities and NGOs to members of local communities - to make sound decisions in the sphere of waste management, using information from the proposed database as a decision-support tool.

It is worth to note that the database of alternative non-incineration waste management technologies is posted at the specially developed web-site. Therefore, the database will be accessible to a broad range of organisations. The database will be permanently updated by descriptions of new technologies.

Organisations, interested in posting information on their R&D works and technologies in the proposed database may do it by completing a relevant questionnaire. However, prior to incorporation of information on newly submitted technologies into the database, the information should undergo expert assessments. Proposed waste management technologies will be incorporated into the database only in the case of a positive conclusion of experts. In such a way, we will be able to control adequacy of submitted information on new prospective technologies.

We hope, that the proposed database of alternative non-incineration waste management technologies will become a reliable and useful source of information that will promote fulfilment of EECCA countries' commitments under many international environmental conventions, allowing to reduce industrial load on the environment.

References:

1. Costner, P., D. Luscombe and M. Simpson, Technical Criteria for the Destruction of Stockpiled Persistent Organic Pollutants. Greenpeace International Service Unit, 1998.
2. Review of emerging, innovative technologies for the destruction and decontamination of POPs and the identification of promising technologies for use in developing countries. The Scientific and Technical Advisory Panel of the GEF United Nations Environment Programme. Final – GF/8000-02-02-2205. January 2004.
3. Reference Guide to Non-combustion Technologies to Remediation of Persistent Organic Pollutants in Stockpiles and Soil. US EPA, Solid Waste and Emergency Response, EPA-542-R-05-006. December 2005.
4. Donnelly, Paul K., Hedge, Ramesh, S., and Fletcher, John S. Growth of PCB-Degrading Bacteria on Compounds from Photosynthetic Plants. Chemosphere. 1994. Vol. 28, N 5. PP. 981-988.
5. Hurt, K. Successful Full Scale Phytoremediation of PCB and TPH Contaminated Soil. The Third International Phytotechnologies Conference, April 19 – 22, 2005, Georgia, Atlanta.
6. Gilbert, Eric S. and David E. Crowley. Plant Compounds that Induce Polychlorinated Biphenyl Biodegradation by Anthrobacter sp. Strain B1B. Applied and Environmental Microbiology. 1997. Vol. 63, N 5. PP. 1933-1938.
7. Interstate Technology Regulatory Council. Technology Overview Using Case Studies of Alternative Landfill Technologies and Associated Regulatory Topics. 2003.
8. Leigh, M., Fletcher, J., Nagle, D.P., Prouzova P., Mackova, M. and Macek. Rhizoremediation of PCBs: Mechanistic and Field Investigations. Proceedings of the International Applied Phytotechnologies Conference. Chicago, Illinois, 2003.
9. Lokhanska, V. Development of Pilot Project "Management and Destruction of Obsolete Pesticides in Pilot Oblasts in Ukraine (Cherkassy and L'viv Oblast)". – Environmentally Sound Management practices on Cleaning Up Obsolete

Stockpiles of Pesticides for Central European and EECCA Countries. – 8th International HCH and Pesticides Forum, May 26-28, 2005, Sofia, Bulgaria.
10. Moklyachuk, L., Sorochinky, B. and Kulakow, P.A. Phytotechnologies for Management of Radionucleide and Obsolete Pesticide Contaminated Soil in Ukraine. The Third International Phytotechnologies Conference, April 19 – 22, 2005. Georgia, Atlanta.
11. Nurzhanova, A., Kulakow, P., Rubin, E., Rakhimbaev, I., Sedlovsky, A., Zhambakin, K., Kalygin, S., Kalmykov, E. L. and Erickson. L. Monitoring Plant Species Growth in Pesticide Contaminated Soil. Te Third International Phytotechnologies Conference, April 19 – 22, 2005, Georgia, Atlanta.
12. White, J. C., Mattina, M. I., Eitzer, B. D., Isleyen, M., Parrish, Z. D. and Gent, M. P.N. Enhancing the Uptake of Weathered Persistent Organic Pollutants by Cucurbita pepo. he Third International Phytotechnologies Conference, April 19 – 22, 2005 Georgia, Atlanta.
13. Zeeb, B., Whitfield, M. and Reimer, K. J. In situ Phytoextraction of PCBs from Soil: Field Study. Third International Phytotechnologies Conference, April 19 – 22, 2005, Georgia, Atlanta.
14. Zharikov, G.A., Varenik, V.A., Borovick, R.V., Dyadishchev, N.R., Kapranov, V.V., Kiseleva, N.I., Kovalyov, V.P., Rybalkin S.P. Ecologically safe technology for bioremediation of soils polluted by toxic chemical substances. - Environmental Aspects of Converting CW Facilities to Peaceful Purposes, 2002. Vol. 37, PP.181-186.
15. Бердичевская М.М., Козырева Г.И., Благиных А.В. Численность, видовой состав и оксигеназная активность углеводородокисляющего сообщества нефтезагрязненных речных акваторий Урала и Западной Сибири //Микробиология. — 1991. — т. 60, N 6.
16. Бобовникова Ц.И., Хакимов Ф.И., Попова А.Ю. Загрязнение окружающей среды г. Серпухова ПХБ, особенности организации мониторинга // Материалы Российской конференции с региональным и международным участием "Национальный план действий по экологически обоснованному управлению диоксинами/фуранами и диоксиноподобными веществами", Репино (Санкт–Петербург), 9–13 июля 2001 г. - М.: ЦМП, 2001 – С. 75-79.
17. Вредные вещества в промышленности. Справочник для химиков, инженеров и врачей. Изд. 7-е, пер. и доп. В трех томах. Том I. Органические вещества. Под ред. Э.Н. Левиной. Л., Химия, 1976.
18. Жариков Г.А. Биоремедиация почв, загрязненных полихлорированными бифенилами // Материалы Российской конференции с региональным и международным участием "Национальный план действий по экологически обоснованному управлению диоксинами/фуранами и диоксиноподобными веществами", Репино (Санкт–Петербург), 9–13 июля 2001 г. - М.: ЦМП, 2001 – С. 116-119.
19. Жариков Г.А., Капранов В.В., Киселева Н.И., Крайнова О.А., Дядищева В.П., Марченко А.И., Дядищев Н.Р., Бобовникова Ц.И. Демонстрационные испытания технологии биоремедиации «in situ» почв, загрязненных полихлорированными бифенилами // Экология промышленного производстваю – 2002. - № 3, С. 48-51.
20. Коронелли Т.В. Принципы и методы интенсификации биологического разрушения углеводородов в окружающей среде (Обзор) // Прикладная биохимия и микробиология. - 1996. - т. 32, N 6.
21. Мельничук С.Д., Шеляженко С.В., Лоханская В.И. К вопросу химического анализа соединений, хранящихся на складах непригодных пестицидов и агрохимикатов во Львовской и Черкасской областях Украины. - Планета без стойких органических загрязнителей (СОЗ): Сборник научных материалов научно-практического семинара в рамках Всемирного дня действий против СОЗ (22 апреля 2005 г., Киев). - К., ВГЛ Обрії, 2005.- 188 с. (С.130-135).
22. Мартынюк А. Н., Скрипник А. П. Применение биотехнологий при комплексной переработке твердых бытовых отходов. Материалы 2-й Международной конференции "Сотрудничество для решения проблемы отходов", 9-10 февраля 2005 г., г. Харьков.
23. МРПТВХ. Научные обзоры советской литературы по токсичности и опасности химических веществ. Минеральные масла. Программа ООН по окружающей среде. ЦМП. Москва, 1982.
24. Скрипник А. П., Дениско П. С. Комплексный подход к переработке ТБО и других содержащих органику отходов с использованием биодинамической технологии. Материалы 3-й Международной конференции "Сотрудничество для решения проблемы отходов", 7 - 8 февраля 2006 г., г. Харьков.
25. Хабаров Ю.Г. Модификация технических лигнинов соединениями железа. Автореферат диссертации на соискание ученой степени доктора химических наук. – Архангельск: изд-во АГТУ.– 2002.– 40 с.
26. http://www.adetech.org
27. http://www.consit.ru, http://www.vnimi.consit.ru
28. http://www.ecolife.pochtamt.ru/
29. http://www.fh.kiev.ua/ru/articles
30. http://inekosorb.com.ua/products/ekolan.shtml
31. www.noharm.org
32. http:// www.sashick.com.ua
33. http://waste.com.ua/cooperation

KINECTRICS NON-COMBUSTION TECHNOLOGIES FOR DESTROYING PERSISTENT ORGANIC POLLUTANTS (POPs)

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1. INTRODUCTION

Kinectrics Inc. (previously Ontario Hydro Research Division) has developed and commercialized PCB destruction/Decontamination technologies. These technologies were first used to manage the large volume of PCB contaminated oil and electrical equipment used in the Corporation. With proven successful record of the international transferring of these technologies to Japan and Korea, Kinectrics sees these technologies as useful tools to assist countries in the implementation of the Stockholm Convention.

Ontario Hydro had, in the early eighties, about 10 million litres of PCB contaminated mineral oil in transformers, had about 1000 metric of Askarel in transformers used in the generating, transmission and distribution system and it also had about 35,000 Askarel filled power correction capacitors.

Without options to deal with this enormous PCB challenge, Ontario Hydro developed first a sodium-based PCB destruction process that could be used to decontaminate the large inventory of this material. In the mid eighties, two mobiles processing units were built. One of them dedicated exclusively for the decontamination of Ontario Hydro's PCB oil; while the second unit was leased to an external company to decontaminate oil from other parties. These units were used to decontaminate and reclaimed near 9 millions litres of PCB contaminated oil in Canada. The chemical process was later optimized to allow for the chemical destruction of pure PCBs.

In the mid 90's, Kinectrics licensed a Japanese company to commercially used this technologies in Japan. Kinectrics' PCB destruction technologies were the first foreign technologies approved for use by the Japanese authorities. Our Japanese Partners were subsequently select to design and built the Toyota City PCB Destruction Plant, own and operated by a subsidiary of the Government of Japan.

Kinectrics also developed a Solvent Extraction Process for the decontamination of PCB contaminated electrical equipment. This process was commercially used in Canada to decontaminate transformers and capacitors containing PCBs. This technology was tested and proved to meet the strict standard for decontamination of PCBs established by the government of Japan.

Kinectrics' technologies, although developed and with an extensive track record for the destruction of PCBs, are also equally effective for the destruction of all other chlorinated persistent organic pollutants covered by the Stockholm Convention.

2. KINECTRICS PROPOSED SOLUTION

Kinectrics has developed, patented and commercialized a number of PCB treatment/decontamination non-combustion technologies that can be used to meet individual countries' needs to meet the requirement of the Stockholm Convention.. Based on the waste streams to be treated, Kinectrics' proposed solution as is follows:

2.1 PCB Contaminated Mineral Oil

For the decontamination of PCB contaminated mineral oil, Kinectrics' proposed solution consists of the design, procurement and installation of a sodium-based PCB destruction system. This technology was originally developed by Ontario Hydro Research Division (Kinectrics' predecessor) and has been used to decontaminate and reclaim near nine (9) million litres of PCB contaminated oil.

Ontario Hydro's process for the dechlorination of electrical insulating oils contaminated with low levels of polychlorinated biphenyls (PCBs) is dependent on the reaction of active sodium with the chlorine in the PCB molecules, under carefully controlled conditions, to form sodium chlorine and hydrocarbon residues.

The principle reaction in the process is the direct removal of the chlorine atoms from the PCB molecule by sodium;

i.e.: $RCl_x + Na^+$-------> $NaCl + R^+_{x-1}$

Where RCl is a PCB molecule containing x number of chlorine atoms (x =1 to 10), Na^+ is a reactive sodium atom, and R^+_{x-1} is a PCB molecule with 1 chlorine atom removed.

R^+_{x-1} is reactive free-radical from the biphenyl structure and combines with H^+ ,formed by the reaction of sodium with water or donated by the mineral oil, to form a neutral RH molecule. If RH contains additional chlorine, it is again attacked by sodium and the process is repeated until all chlorine atoms have been replaced by hydrogen atoms. At this point, the PCB molecule has been converted to a biphenyl molecule and all chlorine atoms have combined with sodium to form sodium chloride or table salt.

Important side reactions which can occur during the dechlorination process include the reaction of sodium with trace water or with acidic organic oxidation products formed while the oils were in service. These side reactions render undesirable acidic oil components insoluble and therefore assist in their removal in subsequent centrifuging and filtering stages.

While the principal organic product formed in the dechlorination reaction is biphenyl, a small amount of an insoluble residue known as Polyphenyls is also produced as a result of biphenyl polymerization. The yield of Polyphenyls increases relative to that of biphenyl as the PCB concentration of the input oil increases. As with neutralized oil acids, this material is removed from the oil in subsequent treatment stages.

Complete dechlorination reaction occurs in both highly concentrated PCB liquid waste (i.e. pure) or low concentration PCB contaminated mineral oil.

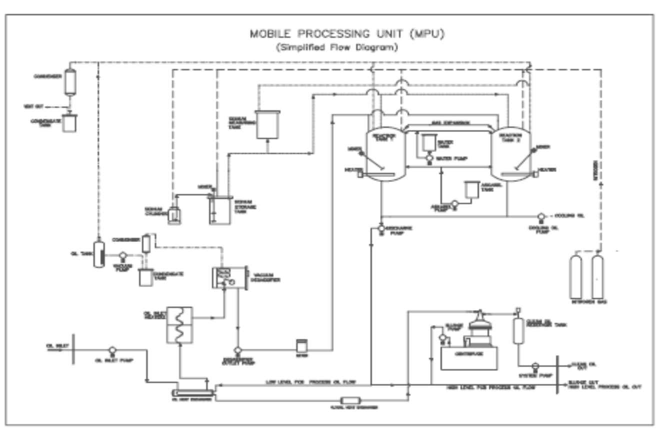
Kinectrics' PCB destruction process is operated as a batch process. Although this mode of operation may reduce the throughput capacity of a similar size system when operated on a continuous mode, there are several practical advantages of the batch process, namely:

- Better emission control. In a batch process the reaction vessel remain close until batch analytical data confirms all PCBs in the reactor has been destroyed. Once the PCB destruction has been confirmed, the reaction vessel is purged with nitrogen during the neutralization of the excess sodium used in the reaction. Obviously, the same level of control cannot achieve on a continuous process.
- The batch operation mode avoid cross contamination of already cleaned oil. As every batch of oil is analyzed prior to evacuation of the reaction vessel, in the batch process everything in the reaction vessel is analyzed. In a continuous processing mode, samples are taken at the different times and if there is fault in the operating conditions, this fault, translated in poor destruction reaction, could be detected only after it has already cross contaminated the already cleaned oil.
- The sodium-based reaction as most PCB destruction reaction, it is an exothermic process. The heat of reaction is quite significant and depending on PCB concentration, could generate enough heat to increase the temperature of the reaction mixture well over the mineral oil flash point. This is even more important when destroying high level PCB liquid waste.

The sodium-based chemical reaction is also applicable to other chlorinated semi-volatile compounds as those identified in the Stockholm Convention.

A simplified diagram of the proposed PCB destruction unit s given in Figure 2.1

Figure 2.1 Simplified diagram of Kinectrics' PCB destruction system for Slovakia.



2.2. PCB Capacitors

One of the major uses of PCBs was in the manufacturing of electrical equipment as the dielectric fluid in transformers and capacitors. In electrical power transformers, the PCBs, mainly Delor 105 and 106 (Aroclor 1254 and 1260 as the US Monsanto Trade names) were blended with tri and tetra-chlorobenzenes to provide the proper viscosity required. In the case of power correction capacitors however, the PCBs were used pure as the dielectric fluid. The PCB type however was the Delor 103 or Aroclor 1242 that with lower chlorine content has a lower viscosity that Delor 105 and can be used without blending as a dielectric fluid in capacitors.

In order to understand the challenges represented by the PCB capacitors, it is necessary to understand their composition and structure. Table 2.1 gives the general composition of 45 kg (100 lb) standard PCB capacitor:

Composition of PCB Power Correction Capacitor

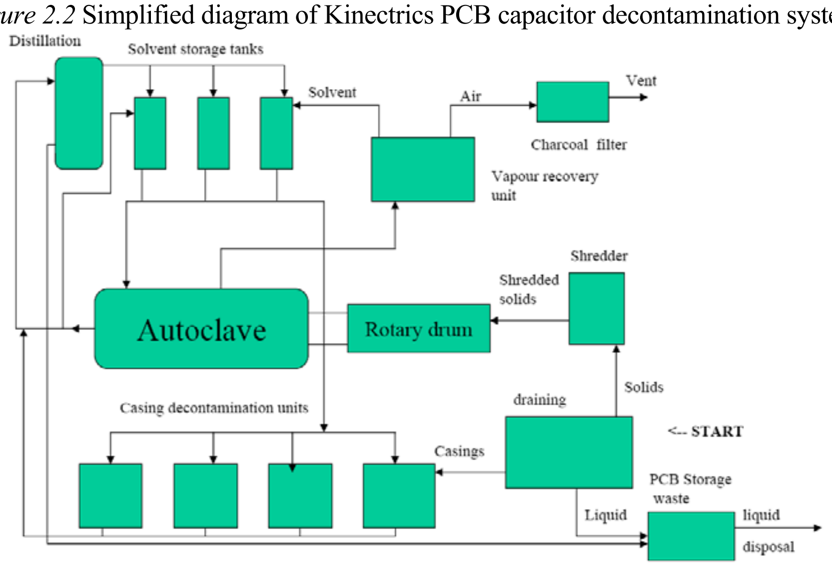
Table 2.1

Component	Percentage Composition (%)	Component Weight (kg)
PCB Fluid	40	18
Metal	20	9
Porous Material	40	18
Total	100	45

The metal components include the casing, wire and electrical conducting surfaces (thin aluminum foils); the porous materials include the paper, a plastic layer and rubber gaskets and insulator. The metallic foil, insulating paper and polymer layer are rolled up in a coil fitted with contact wire leading out of the capacitor. In the case of a PCB capacitor, the dielectric fluid is usually Delor 103 (Aroclor 1242 or 1016 in North America.

Kinectrics' proposed solution for treating the PCB capacitors consists of draining the PCB liquid, separating the capacitor into its major components (casing and core), and using a solvent extraction procedure to remove the PCB from the solid components.

Figure 2.2 Simplified diagram of Kinectrics PCB capacitor decontamination system



3. PCB DESTRUCTION EFFICIENCY

Kinectrics' Sodium-based is an efficient chemical process for the destruction of PCBs and other halogenated materials, including all persistent organic pollutants included in the United Nations Stockholm Convention.

Analytical results from different, independent laboratories have confirmed the consistency and completeness of the PCB destruction reaction. Operated as a batch process and a close system, all PCBs are totally destroyed before the reaction before is re-open and the cleaned oil/byproduct removed from the reactor. The final concentration of PCBs from the treatment of low level PCB contaminated mineral oil or the destruction of pure PCBs is essential the same, non-detection of PCBs in liquid phase, solid (sludge) or in the air emission streams.

the Destruction Efficiency is defined as:

Equation 1:

$$DE(\%) = \{(totalPCBin) - (totaPCBout)/(totalPCBin)\} * 100$$

Because of the best available analytical technique, High Resolution Mass Spectroscopy, has a minimum detection level of 1 to 4 ug/kg for PCBs in oil and 0.036 ug/kg of PCBs in sludge, the minimum DE of 99.9999% cannot be demonstrated when any PCB destruction technology is used to treat PCB contaminated mineral oil.

The six nines PCB destruction efficiency can only be demonstrated when destroying pure PCBs. The data included in the experimental program carried out by Kinectrics Inc. to demonstrate its sodium-based PCB destruction process meets Japanese Regulatory requirements can be used to confirm the minimum 99.9999% Destruction Efficiency for this technology. The test results summarized in the Japanese Association of Industrial and Environmental Management/1/ were used to demonstrate the Kinectrics' PCB destruction process ability to meet the minimum 99.9999% DE.

The demonstration program for the Japanese government included five PCB destruction runs, namely two runs using PCB contaminated mineral oil (~ 100 ppm) and three runs using pure or high level PCB wastes (Table 5, page III-19). Runs 3-1 and 3-2 were carried out using a blend of pure Aroclor 1242 (Delor 103) and transformer Askarel containing Aroclor 1260 (Delor 106) and tri- and tetra-chlorobenzenes. Table 5 in the Japanese report (page III-50) provides an explanation of the numbering system used throughout this report. Thus the results for runs 3-1 and 3-2 are referred in Maxxam Laboratories report as runs 2-1 and 2-2 respectively.

The results for residual PCB concentration in the oil phase (liquid) are given in pages III-102 and III 103. It is observed that the residual PCB content in the oil phase is below the minimum detection level for all congeners analyzed. Table 1 summarizes the results for the residual PCBs (isomer groups) for the liquid phase.

The results for residual PCB concentration in the sludge (solid phase) are given in pages III 183 and III-184 of the report. For the solid phase, it is also observed that the residual PCB concentration is below the minimum detection level for the analytical technique. These results have also been incorporated into Table 1 below.

Analytical results for oil (liquid) and sludge (solid) phases for high level PCB destruction experiments

Table 1

ISOMER	**Liquid MDL**	**Sludge MDL**
	μg/kg	μg/kg
Monochlorobiphenyl	1	0.036
Dichlorobiphenyls	1	0.036
Trichlorobiphenyl	1	0.036
Tetrachlorobiphenyl	4	0.036
Pentachlorobiphenyl	1	0.036
Hexachlorobiphenyl	1	0.036
Heptachlorobiphenyl	1	0.036
Octachlorbiphenyl	1	0.036
Nonachlorobiphenyl	1	0.036
decachlorobiphenyl	1	0.036
SUMM	**13**	**0.36**

Air PCB emissions were also determined during the PCB destruction experiments. Table "PCB Congeners in air (pages III-173 and III-174) shows that the PCB emissions, after the air pollution control system, in the destruction unit (Maxxam ID 141044 and 141046) for runs 3-1 and 3-2 were below the detection level of

30 nanograms for the analytical technique. With 10 possible isomer groups, the total PCB emission from these experiments was < 300 nanograms.

Summary of PCB injection and final PCB concentration for High Level PCB destruction experiments

Table 2

RUN #	Aroclor 1242	Aroclor 1260	Total PCBs	Chloro benzenes	Total Chlorine	Final PCB in Liquid	Final PCB in Sludge	Mass of Oil	Mass of Sludge	Total PCB air emission
	(kg)	(kg)	(kg)	(kg)	(kg)	µg/kg	µg/kg	kg	kg	ŋg
						All Isomers	All Isomers			all isomers
3-1	14.8500	1.1220	15.9720	0.53	7.23	<13	<0.36	766.044	398.16	<300
3-2	14.8500	1.1220	15.9720	0.53	7.23	<13	<0.36	766.044	398.16	<300

The analytical results and the mass of oil and sludge allow the quantification of the total PCB residual in each byproduct stream. Table 3 summarizes the amount of residual PCBs in the sludge, oil and air streams.

Residual PCBs in the sludge, oil and air streams for PCB destruction experiments 3-1 and 3-2.

Table 3

Run #	Residual PCBs in sludge	Residual PCBs in Oil	PCBs air emission	Total un-reacted PCBs
	µg	µg	µg	µg
3-1	143.3376	9958.5200	0.3000	10102.16
3-2	143.3376	9958.5200	0.3000	10102.16

With the data in Table 3 and using equation 1, the Destruction Efficiency for Kinectrics' Sodium-based PCB destruction technology can be calculated. The results are summarized in Table 4.

Destruction Efficiency for Kinectrics' Sodium-based PCB Destruction Process

Table 4

Total Initial PCBs	Total Initial PCBs	Mass of Residual PCBs	PCBs Destroyed	Total Destruction Efficiency
kg	µg	µg	µg	%
		Less than	Greater than	Greater than
15.9720	15972000000	10102.16	15971989898	99.99993675
15.9720	15972000000	10102.16	15971989898	99.99993675

4. Conclusions

Kinectrics PCB destruction/decontamination technologies are:

- Environmentally friendly, as they converted toxic contaminated materials into reusable commodities, selectively destroying the PCBs without emissions.
- Efficient, as they have been demonstrated to destroy PCB wastes, completely exceeding the minimum 99.9999% destruction efficiency, normally required in incinerator.
- Economical, as these technologies can process PCB contaminated waste at similar or lower cost than incineration alternatives.
- Convenient and versatile, as they can be designed as mobile or fixed systems, to meet the needs of the clients.
- Proven, as many years of international experience have demonstrated consistent performance, meeting most restrictive regulatory requirements.

References:

1. Japanese Association of Industrial and Environmental Management, "Persistent Organic Pollutants: Evaluation of Treatment Technology Report, Ontario Hydro Sodium Method", Japan, 1998.

ALTERNATIVE PLANT PROTECTION STRATEGIES HOW TO AVOID PESTICIDE-DERIVED ENVIRONMENTAL THREATS

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The common practice of pesticide use in modern agriculture carries several dangers. Problems like bioaccumulation of Persistent Organic Pollutants (POPs) in animals and man, discharges of poisonous substances into ecosystems, agent residues in food and contaminated feed and thus threats to human health need to be discussed with regard to long-term effects. A feasible way to completely avoid the application of synthetic pesticides in plant protection is the use of and cooperation with natural regulation processes in agricultural production by implementation of organic farming principles. The authors propose the conversion from conventional farming to the ecologically, socially and economically sound and sustainable practices of Organic Agriculture. Especially worth mentioning is its potential for the reduction of fossil fuel consumption and thereby contributions to the mitigation of climate change.

Key words: Pesticides, organic farming, agroecosystems, agrobiodiversity, natural processes, soil health, external costs.

Introduction

Modern intensive agriculture uses pesticides in order to obtain the highest possible economic yields, as well as to contain the further dissemination of all kinds of phytopathogens in agroecosystems and the foodstuff, respectively. Walking along with the pesticide use are threats for the safety of drinking water, soil health and the health of humans and animals. A well known – and not at all new - approach that can help to avoid the use of pesticides and agrochemicals in general, and, through this, to exclude to a great extent the probability of contaminations with agent residues is Organic Agriculture (hereinunder, OA). As OA does not depend on external inputs as much as the conventional agriculture, organic farmers become more independent, regarding their economic and social situation. Furthermore, externalities for the society can be avoided. The general principles of this agricultural system will be shown in this article and the potential for reduction and avoidance of synthetic pesticides will be pointed out.

Description of general principles in Organic Agriculture

OA is a holistic approach, considering a farm as a living organism with close interdependencies between the most essential elements needed in agriculture: soils, plants and animals. In OA these natural resources have to be integrated into a "closed cycle", a circuit to generate and to sustain their health and productivity. The organic approach emphasises ecosystem management practices rather than external agricultural inputs. The avoidance of chemical fertilizers and chemical pesticides is a major principle.

Organic farmers have to promote an optimal balance in interactions between soils, plants and animals which produce precious natural fertilizer. Legumes collect and store plant nutrients and provide animal fodder as well. Crop rotation influences and regulates soil fertility, soil structure, disease resistance and leads to economic risk minimisation through crop diversity. Crop rotation systems have to interact with existing or newly established landscape elements and the relief and exposition as well. Wild biodiversity and agrobiodiversity support self regulation mechanisms in plant growth and the maintenance of genetic diversity. The ban on genetically modified organisms in organic production prevents adverse health effects for both animals and humans. Animals are treated in a responsible manner, according to their natural behaviour needs. Organic animal healthcare tries to avoid the preventive use of antibiotics that, on the one hand, mean possible residues in food and spread over the farm by the animals' excretions, respectively.

In order to secure transparency for consumers and to have common conditions for the farmers' access to markets, regulations on private and governmental level were established. Standards for private associations are described at international level through the IFOAM[1] Basic Standards as a common agreement about what

[1]International Federation of Organic Agriculture Movements

an "organic" claim on a product means. These Basic Standards also gave orientation for Organic standards codified in technical regulations of governments, like the EU, Switzerland, Norway, USA and Japan. The European Unions *Regulation on Organic Production and Labelling of Organic Products* not only sets standards for production but also for processing and marketing e.g. for labelling. Countries which have their own law on organic production often run programs supporting farmers to convert to OA and to maintain it. Especially during the period of conversion state-sponsoring can influence farmers´ decisions. Control of adherence to the standards and certification of farms and processors is carried out by state-run or independent certification bodies.

Plant protection approaches in organic farming

Organic farmers, due to the restricted toolbox (ban on synthetic substances), on the one hand, and because of their awareness of natural processes likewise, need to think "Protection" in a different context than conventional farmers do. Possibilities to contain any kind of pest by direct actions are limited and interventions have to be implemented on a different level. Most important in this context are management actions that, contrary to conventional farming, can not and do not intend to kill all phytopathogens. OA uses a system-oriented approach.

To secure safe feed, food, as well as healthy plants and adequate yields, organic farmers strive for balanced methods and therefore first try to influence the equilibrium between pests and their antagonist organisms. These methods are defined as "management measures" and will be explained after a short explanation of two other pillars in organic plant protection.

A second component of plant protection as a preventive strategy is the promotion of pathogen resistant varieties in plant breeding without the use of genetically modified organisms. Plant breeders, farmers unions or seed pools are vital in this context because breeding is rather complicated to tackle on single farms and bears many risks that can thereby be spread on many shoulders. The third pillar of organic plant protection that does as well need to be involved in the farmer's management at field level is the direct method known as biocontrol. This comprises the dissemination of beneficial organisms (antagonists of plant-pathogens) and the use of so-called biopesticides and plant health enhancers. They are substances of vegetable raw-materials, of microbial and mineral origin and, in the case of mating-disrupting pheromones, artificially produced. Additionally to the restricted derivations, stakeholders in organic farming like farmers-associations and regulation bodies govern the use of these substances by the help of lists of supported products considered as natural, completely degradable and correspondent to OA principles.

Still, the most important pillar is the well-balanced ecosystem and, hence, indirect medium-term and long-term measures that combine three major preventative strategy-components, as follows:

<u>Inclusion of landscape components:</u>

Natural conditions are considered as parameters man has to respect and involve into his agricultural actions. Land improvement measures concerning soil properties are only applied through draining or ploughing, by lime and powdered rock in some cases. Plots near waterbodies will not be cultivated but used as grassland to avoid eutrophication. The central element is the creation of (or to leave untouched) habitats for natural enemies species. Thanks to the positive effects pest-antagonists have on the stability of agricultural production, this even affects farms accountancy. Especially if these habitats are situated on the least productive parts of the farm and correspond with woods and hedgerows. By this not only functional biodiversity is enhanced, but micro- and macro climate can be influenced and wind and water erosion processes will be attenuated. Further stabilization of soils is accomplished by the combination of hedges, strips of grassland and tillage along the contour lines.

<u>Cultural practices:</u>

Each season decisions concerning the compound of cultivated crops affect the conditions that either promote or contain pathogens. Most common are longer crop rotations that limit the occurrence of host plants and the choice of tolerant and / or resistant varieties. In a lot of countries the availability of high quality seeds is a major obstacle regarding crops' competitiveness and thus a main reason for the application of pesticides. Regarding a farmer's prospects to control plant diseases, not only rotation criteria have to be accounted; location of plots and distances from field to field are important as well. Permanent crops like orchards and vineyards can be kept safe and sound by wider spacing.

Vegetation management:

In this context, cultivation of soil and weeding are the most important measures and they allow a more direct intervention. Further actions on a shorter time-horizon are the shift of sowing and harvest time or the promotion of host plants targeted to enhance natural enemy's impact. Closely related topics which also touch other fields of the organic farm are the use of organic fertilizers to nourish competitive soil organisms, the modification of distances between rows and in-between in order to ameliorate the micro climate in crops.

The benefits of Organic Agriculture in a broader context

As displayed above, OA can help to totally avoid the use of synthetic pesticides and POPs that are harmful for our environmental and personal health. Success stories from all over the world show that OA is a feasible method to establish a stable agricultural system that can not only help to abolish the use of dangerous substances in a farmer's everyday life and their discharge into adjacent ecosystems. Over and above, OA can help to tackle global problems like food availability, food safety and security (ZUNDEL et. al., 2007). Furthermore smallholder families can achieve higher resilience regarding economic risks and natural disasters. Organic farmers are highly aware when it comes to environmental issues and the interdependencies between agricultural production and natural processes.

Comparison of two Approaches in agricultural systems

Table 1

System	**Organic Agriculture**	**Integrated Production**
Approach	Holistic, general ban on chemical-synthetic substances	Concept of economical damage threshold
Application of (in order of importance)	1. MANAGEMENT MEASURES - *Inclusion of landscape components in agroecosystems* - *cultural practices* - *vegetation management* 2. PROMOTION OF PATHOGEN RESISTANCE IN PLANT BREEDING 3. BIOLOGICAL CONTROL - *(vegetation management to enhance natural enemies impact)* - *dissemination of beneficial organisms* - *non-synthetic pesticides (plant-derived, microbial or mineral origin)*	1. MANAGEMENT MEASURES (to certain extent only!) - *Consideration of landscape components* - *cultural practices* - *vegetation management* 2. USE OF PESTICIDES, in order to obtain highest possible economic profit (profit maximisation) 3. PROMOTION OF PATHOGEN RESISTANCE IN PLANT BREEDING 4. BIOLOGICAL CONTROL (to certain extent, sensitive areas like greenhouses)
Negative effects **Farm** **Society** **Environment**	 Higher workload, less specialisation More land needed for same production Intense soil working might lead to nutrient leaching and erosion	 Accumulation of pesticide stockpiles High external costs, agent residues in food Less biodiversity, restricted ecological niches
Benefits **Farm** **Society** **Environment**	 Risk reduction by diversification, no dangerous substances Lower external costs, people's health Higher biodiversity, ecological niches	 Higher specialisation, lower workload, easy management Low food prices Various negative effects on local and global scale

Based on the plant protection concept displayed above and the scientific research that shows how organically managed soils feature a higher activity of microbial biomass (MÄDER et. al., 2002), a key for nutrient management, soil health and soil stabilization that results in lower erosivity, the ecological amenities are obvious.

In transition countries, most of the southern hemisphere and also in disadvantaged regions of wealthy states, the conversion to OA gives farmers the opportunity to achieve economic results that are comparable or even better than those of their conventional counterparts. This is especially important, where environmental concerns are not considered because of poverty and hunger. There is no necessity for and no more dependency on intermediate inputs like fertilizers and pesticides. Another reason for a good economic performance is the spreading of risks on crop rotations, related animal husbandry and agroecosystems that can compensate threats – healthy soils are the key issue again. If we concentrate our attention on social issues, aspects like the care for our companion animals and the preservation of a liveable environment have to be named. Likewise, the end of dependency on external inputs with unpredictable price development and uncertain long-term effects on our health – spread through environmental mechanisms or as residues in food and feed - is a major reason for OA's preferableness.

Three more points, situated between economic, ecologic and social criteria need to be mentioned here: One is the issue of subsidized surplus production in wealthy countries. With OA these countries could cut down their expenses for export subsidies (which they will anyway have to, according to WTO agreements), reduce the level of agricultural output to a healthy state and end the unjust conditions of the world's markets.

Secondly, agriculture, as we know it today, is highly dependent on the input of fertilizers. To obtain them and process them to an appropriate state, we require high energy inputs (for synthesis and exploitation) or the shipping of animal feed (nutrients as well!) around the globe. With rising prices for energy and thus for transportation and processing, these practices will become very questionable in the foreseeable future. Eutrophication of ecosystems in areas with high livestock rates or feed lots, as well as the biomass-fishing practices for feed production are both socially and environmentally out of the question.

A third issue is the so-called internalisation of external costs. Difficult to quantify though, scientific studies (PRETTY et. al., 2000) show that, taking into account the negative side effects of modern conventional agriculture, the aforementioned needs to be disestablished. There are indications that in certain countries the social costs for the remediation of water, the loss of soil health, pesticide discharges and other pollutions summed up would by far exceed the social benefits of the whole agricultural sector.

Organic Agriculture is a sustainable form of agricultural production and a feasible way to avoid environmental impairment

As demonstrated above, the authors consider OA as a role model for the agriculture of decades to come. It strongly corresponds to sustainability criteria. Technical problems, like nutrient recycling or their availability for plant roots can be solved through research and optimization of already existing processes. Attempts like biological pest control point into the right direction but need to be involved into the holistic approach of OA in order to keep the intensity and frequency of interventions as low as possible. Most important is the awareness of consumers as the final profiteers of healthy food and a sound environment. In the end they are the ones who, supported by politicians, can facilitate or force agriculturists to change or modify their production processes. We suppose that OA should, after a period of conversion and an intermediate state like Low Input Sustainable Agriculture, be implemented worldwide. Considerably lower external costs, the cooperation with natural processes and thus a planet worth living on is not only a concept, but a desirable heritage to forthcoming generations.

References:

1. Mäder, Paul; Fliessbach, Andreas; Dubois, David; Gunst, Lucie; Fried, Padruot und Niggli, Urs (2002) Soil Fertility and Biodiversity in Organic Farming. *Science* 296:pp. 1694-1697.
2. Pretty, J.N. et al (2000). An assessment of the total external costs of UK agriculture. Agricultural Systems,. 65, pp 113-136.
3. Zundel, Christine; Kilcher, Lukas (2007) Organic Agriculture and Food Availability, Article at the Conference: International Conference on Organic Agriculture and Food Security, Rome, Italy, May 3-5, 2007, http://orgprints.org/10753/ (2007/08/06).

DETOXIFICATION OF POPs WASTES, DIOXIN, PCB AND AGRICULTURAL CHEMICALS BY MECHANOCHEMICAL PRINCIPLE

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Radicalplanet technology is the complete detoxification method that changes POPs wastes, chlorinated organic compounds, into safety compounds under non-combustion, atmospheric and closed conditions by using of the mechanochemical principle. As the admixture of the POPs wastes, there are concrete brocks, soil, glass, metal (cans and pipes), plastic masks, clothe, work gloves, protective clothing, chipped wood, cardboard paper, pieces of plastic goods PP, PVC and liquid or emulsion in the bottle, such as oil and organic compounds. While the Pesticides, Dioxin, PCB, and related POPs wastes are treated, there are neither exhaust gas nor effluents at all. There is no fear of secondary pollution and this process is guaranteed clean conditions. When the physical energy is exerted greater than a specific strength, the organic chlorinated compounds will be chemically activated. The bond of each molecule is cut by mechanical energy and decomposed into the activated state, called the radical state, after then chemical reaction is accelerated. Safe and less expensive additives, such as CaO, are selected as dechlorination agent in this treatment. After the detoxification treatment, the toxic equivalent value became below 1pg-TEQ/g. The destruction removal efficiency was over the 99.9999%. The chlorines combined with CaO-radical and formed chlorinated inorganic stable compounds, such as $CaCl_2$. It is confirmed that the final product is quite safety by the method of Bioassay valuation. In this process, 500-1,000 ton of POPs wastes will be treated in a year, by using one unit of the equipment. The safety of this process will get the community and public acceptance. This radicalplanet technology was officially granted in April 1, 2004, in Japan. The authors have already a practical scale machine in Japan. In future, the non-combustion process will be an alternative destruction technology of incineration.

Key words: Mechanochemical, POPs wastes, Non-combustion, Detoxification, PCB, Agricultural chemical, Dioxin, Radicalplanet technology.

Introduction

Recently it is widely recognized that the chemical reaction occurred by the mechanochemical principle.[1] We paid attention to some reports that the man-made negative legacy could be detoxified safely and completely. We constructed the practical machine and proved that harmful chloride compounds converted into safety inorganic materials by using this practical machine. As the target organic compounds, PCB oil and stabilizer contaminated by PCB and POPs wastes (BHC, Chlordane, Endrin, etc.) were selected.

Experimental Method

Experiments were carried out in a practical-scale planetary ball mill holding three vessels (each capacity is 250L) contained steel balls. Figure 1 shows the schematic profile of the pilot-scale E-200 type system. The each rotational speed, three reaction bawls and base, was 70 rpm (~100 rpm: practical use), conversely and constantly during the detoxification reaction.

Fig. 1 Schematic Profile of E-200

1. Dioxin (Polluted soil and ash): The toxic equivalent of dioxins contained in the polluted soil was 7500 pg-TEQ/g, and that of dioxins contained in the fly ash was 6900 pg-TEQ/g. The soil and ash were put in the thick-paper bags.

2. PCB: The PCB (53.6%PCB+38.4%Trichloro-Benzene) in the bottles, and some stabilizers contained PCB were treated by using the dechlorination agent, CaO (burnt lime). PCB oil was put in the glass bottles and stabilizers containing PCB were put as these are.

3. Agricultural Chemical: The agricultural Chemicals contained BHC

(5%BHC), Chlordane (42%), DDT (5%), Endrin (2%) and PCNB (20%) were treated with the dechlorination agent. Agricultural chemicals were put in the vinyl bags or in the glass bottles.

Table 1 shows the distribution ratio of the dechlorination agent to the polluted soil and ash, to the PCB Oil and stabilizers and to the agricultural chemicals.

Table 1 Distribution Ratio of Detoxification Agent (Lime or B.F. Slag)

	Dechlorination Agent / Target (weight)	
	Experimental Distribution Ratio	Suitable Distribution Ratio
Aim	Limtation(Final Value) Measurment	Practical Treatment
Dioxin / Soil*	4 ~ 6/1	3/1
/Ash*	4 ~ 6/1	3/1
PCB /9.6%PCB	25/1	12/1
/0.8%PCB	12/1	6/1
/Stabilizer	6/1	3/1
Agricultural Chem.*	3 ~ 12/1	3/1
*:Lime/B.F.Slag=2/1		

Table 2 Composition of Lime and Blast Furnace Slag

	CaO	SiO2	Al2O3	MgO
Lime	95.1	0.9	0.8	1.4
B.F. Slag	42.4	33	14.5	6.5

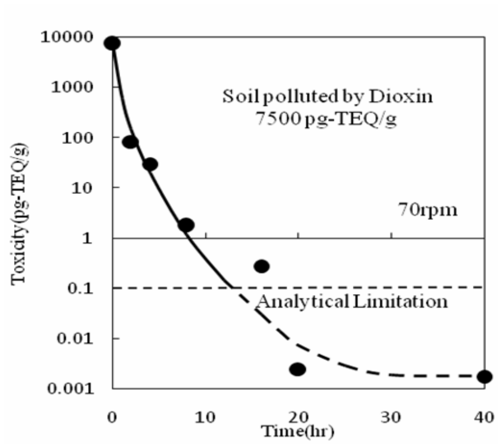

Fig. 2 Behaviour of Toxicity (Soil polluted by Dioxin)

The distribution value was decided by the condition of test. In the case of measuring the limitation value, the distribution ratio was increased to high revel. In order to decide the suitable ratio, the some samples were taken out during the treatment period, and we selected the most suitable distribution ratio. The dechlorination agent were burnt lime and blast furnace slag and those contents are shown in Table 2. In these experiments, samples were evaluated toxic equivalent by the concentration of dioxins and Co-PCB. The analysis is according to "Soil Investigation Tentative Manual that affects Dioxins"(release from Environment Agency) and "Manual of Method for Determining Toxic Matters caused by Atmospheric Pollution"(release from Environment Agency). In addition, Toxicity Equivalency Factors (TEQ) is according to WHO-TEF (1997).

Experimental Results and Discussions

(1) Detoxification reaction

The behaviors of the toxic equivalent during the rotational period are shown in Fig.2 (Soil Polluted by dioxin), Fig.3 (51.3%PCB+38.4%Trichloro-Benzene) and Fig.4 (3%BHC emulsion) respectively.[5] It was found that the dioxin toxic equivalent decreased with the increase of the grinding (chemical reaction) time in each case. After about 5 hours, the dioxin TEQ decreased less than 10pg-TEQ/g (the analytical limitation, non detected level, is about 10pg/g). After 8 hours, the toxicity of Co-PCB reduced less than 0.01pg-TEQ/g. The dechlorination ratio reached above 99.9999% in the treatment of target compounds and organic-chlorine compound was never detected. As the result of investigating these data, it was estimated that the decomposing speed will be increased twice and that the detoxification time will be reduced by half with increasing the rotational speed (in case of 100rpm). However the decomposing speed will be decrease with increasing the amount of target and the concentration of target, as shown in PCB and BHC, the dechlorination reaction proceeds rapidly and reaches less than the analytical limitation.

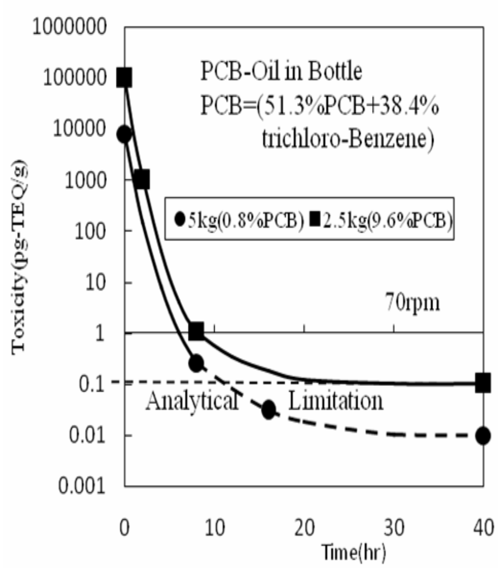

Fig. 3 Behaviour of Toxicity (51.3%PCB-Oil)

In the practical process, it is very important that the suitable conditions should be chosen, a rotational speed, steel ball conditions, an amount of target, a concentration of target, a ratio of CaO and so on.

(2) By-Product

(a) Safety

As the dioxin toxic equivalent of the soil and ash become less than 10pg-TEQ/g after treatment of this process, the powdered soil is both safety and is able to reuse for high strength and hard materials after solidifying the powdered soil with water.[3]

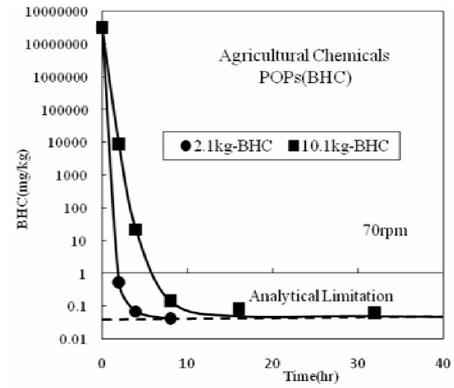

Fig.4 Decomposition of Agricultural Chemicals(BHC)

(b) Reaction Mechanism in PCB Destruction.

As all of the organic chlorine of PCB become to inorganic chlorine after treatment of this process, the organic chloride-compounds can be dissolved out from the powdered by-product with a normal suitable solvent. It was confirmed that the organic compounds were constituted from the hydrogen-reduction of Biphenyl, Terphenyl, Quarterphenyl, and lower molecular hydrocarbon (alkane, alken, benzene, toluene and lower molecular poly-cyclic aromatic hydrocarbons).[4, 6] The results of the more detailed analysis, we are convinced that the ring of benzene was cut to the separated state and became to the radical state.

GC/MS-SCAN: Toluene, styrene and some kinds of esters were observed by extracting with ethyl acetate. Benzene, ethyl dimethyl benzene and some kinds of aldehyde were observed by extracting with toluene.

GPC: The molecular weight of organic compounds extracted with Ethyl acetate or Toluene were in the region of 1400 ~ 200 by converting into the polystyrene molecular weight. The strong peak was 269 at the instruction with Ethyl acetate and was 168 at the instruction with Toluene. The molecular weight decreased to the region of 64 ~ 596 by extracting with Toluene after washing the sample by nitric acid, and the amount of extracted compounds decreased with proceeding of the chemical reaction.

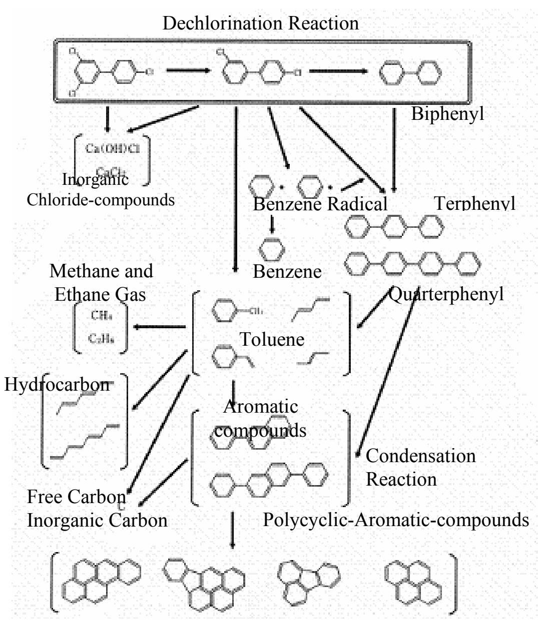

Fig.5 Estimation of PCB Destruction Mechanism

GT-DTA: The existence of the free carbon was confirmed in the remnant, which remained after washing by nitric acid and extracting with Toluene. The free carbon was estimated an inorganic compound. The weight of free carbon was calculated, a few percent, by the weight loss in burning at the atmospheric condition, after burning at the nitrogen condition. The amount of the free carbon increased with proceeding of that reaction.

IR: The absorption peaks originated in carbon hydrate were observed in the region of 2920 cm^{-1} and 2850 cm^{-1}, those in aromatic compounds were 1520 cm^{-1} and 760 cm^{-1} and that in fatty acid was 1700 cm^{-1}.

NMR: The absorption peaks originated in proton of carbon hydrate residue were observed in the region of 0.9ppm, 1.3 ppm and that originated in proton of aromatic compounds was observed in 6.7 ~ 7.2ppm.

GC/MS (Gas contents): The methane, ethane and benzene were observed in the vessels during the chemical reaction. The amount of these gases decreased with proceeding of the chemical reaction and these gases were never observed at the end of reaction. It was estimated that these gases were absorbed and combined with the great fine powdered particles.

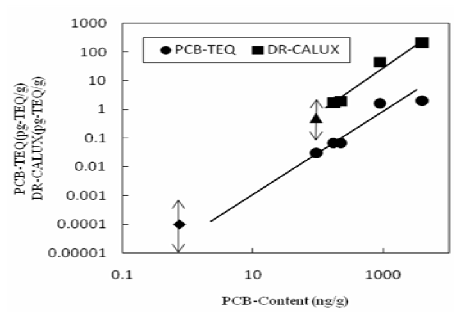

Fig. 7 Relation between -PCB Content and PCB-TEQ , DR-CALUX

On these detail analytical data, the decomposition reaction mechanism was estimated and shown in Figure 5. As concerning o confirmed that the organic compound is completely safe both b method of DR-CALUX (Bioassay valuation). Figure 6 shows tha correlation. Then the by-product of PCB treatment is safety by the the way, the inorganic-chlorine compounds in the by-product c become to safety salt water-solution. The powdered solid of by-p after solidifying with water, in much the same way as by-product of

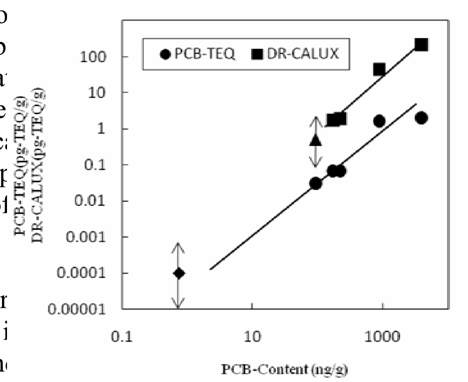

Fig. 6 Relation between -PCB Content and PCB-TEQ , DR-CALUX

Practical Use

From the above experimental results and the estimated dechlor mechanochemical process, called to "Radicalplanet technology" i detoxifying the soil and ash polluted by dioxins, the PCB Oil an chemicals called POPs. This technology is new non-combustion POPs wastes treatment and is officially granted by the notification a

(1) Chemical reaction speed

In this process, the chemical reaction speed is responded on the amounts and shape of target, the amounts and ratio of additional material (the detoxification agency), the rotation speeds of axis and orbit, the amounts and size of steel ball, and so on. For example, the total inner volume of vessels is 750 liters at the E-200 type and the amount of target is estimated about one half of the volume, 370 liters.

(a) Amounts and shape of target

At first, as the target should be put into the each vessel, the size of the target must be smaller than the diameter of the vessel, the volume must be smaller than 370 liters and the target may be packed in paper or vinyl bags, in glass or metal cans.

(b) Amounts and ratio of additional material (the detoxification agency)

As for the detoxification agency, the molecular weight of CaO, theoretically, must be greater than the weight of two chlorine atoms. In order to occur the dechlorination reaction, the additional amount of the detoxification agency may have better to use far more than the theoretical one. The amount of detoxification agency should be decided in a manner that is appropriate and effective. At the practical process, the amount of that was selected as three or six times. By the way, in the case of POPs wastes, the amount of the detoxification agency should be even or twice as much as the whole weight of POPs wastes.

(c) Rotation speeds of axis and orbit

Usually impact energy varies as the value of raising the rotation speeds to the second power. When the rotating speed will be 100rpm at the practical process, the dechlorination reaction speed may increase by approximately twice and the final treating time will be reduced by half.

In order to accelerate the chemical reaction speed, the authors had better to increase the rotational speed of Machine and to supply something into the vessels. It is possible to shorten the detoxification time to one quarter by increasing the rotational speed twice.

(d) Amounts and size of steel ball

It is very difficult to select the amount and size of steel ball. The selection of steel ball has direct effects upon the dechlorination reaction speed and the maximum impact energy. The practical machine, E-200, is scarcely fit for use. The suitable size is 26-45 inches diameter.

(2) Treatment of POPs wastes

The safety is very important factor at the practical use. The polluted materials never expand, because this process is a closed system and never occur the exhaust gas and effluents during chemical reaction. The safety of this process will get the community and public acceptance.

In future, the non-combustion process will be an alternative destruction technology of incineration.

(a) Category of POPs wastes

As the admixture of the POPs wastes, there are concrete brocks, soil, glass, metal (cans and pipes), plastic masks, clothe, work gloves, protective clothing (tyvex), chipped wood, cardboard paper, pieces of plastic goods PP, PVC and liquid or emulsion in the bottle, such as oil and organic compounds. This mechano-chemical process (Radicalplanet Technology) is most suitable for the POPs wastes treatment, because of non-heating, safety, low cost and reliability.

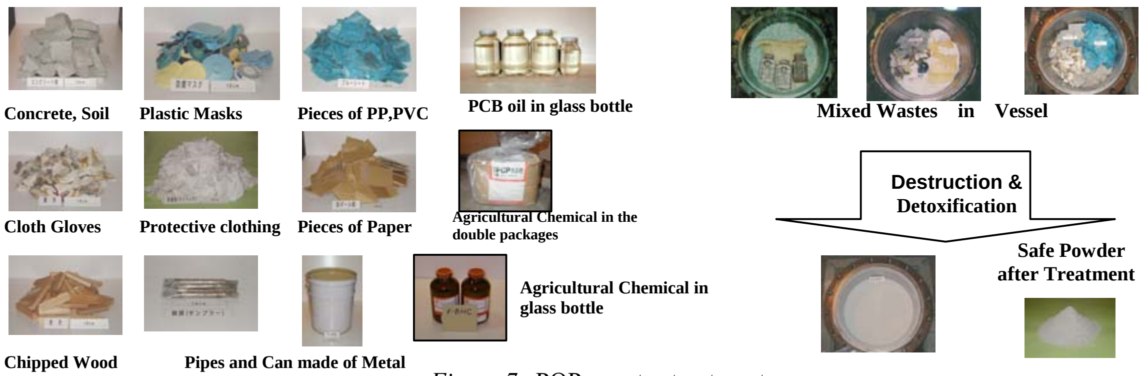

Figure 7. POPs wastes treatment

(b) Capacity of practical treatment

When the much wastes should be treated, such as soil, protective clothing and masks, the authors will recommend using one unit of equipment which is consisted of three machines, because these machines will be operated at high efficiency by shift, for example two operating by three machines. The authors recommend to using this Radicalplanet Process in order to treat in safety the soil and ash polluted by dioxins (10ng-TEQ/g), 1000 t/y per one unit of the equipment. On the case of PCB wastes (stabilizer), this process can be treat 500 t/y per one unit of the equipment. On the case of POPs wastes (with BHC content of 0.1%), this process can be treat 250-500 t/y per one unit of the equipment. The capacity of this process may be different from density of materials and the concentration of the pollution.

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References:

1. A.K. Hall, JM Harrowfield, RJ Hart and PG McCormick. Environmental Science & Technology 1996;30:3401.
2. K. Shimme, T. Akazawa, T. Matsuo, F. Saito, J. Kano. Resources Processing Society of Japan 2001; 48:238.
3. K. Shimme, T. Akazawa, H. Yamamoto, J. Kano, F. Saoto. World Congress on Particle Technology 4 2002; 406.
4. K. Shimme, Y. Deguchi. Resources Processing Society of Japan 2003; 50:209.
5. K. Shimme. Environmental Solution Technology 2005; 31:16.
6. K. Shimme, K. Takase, K. Shiozaki, Y. Deguchi, A. Okawa. In: Sentan Funsai gijyutsu to ouyou, Association of Powder Process Industry and Engineering, Japan (ed.), NGT Press, Tokyo, 2006:502.

THE ACTUAL FATE OF HCHs AND OTHER OCPs IN THE CZECH REPUBLIC

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Persistent organic pollutants (POPs) including organochlorinated pesticides in all environmental matrices are studied and monitored in the Czech Republic round twenty years. Important part of these studies is a long-term monitoring in the area of the observatory in Košetice which is developed as regional background monitoring site in the Central Europe. The monitoring of POPs is performed on the base of integrated monitoring approach. Results of long-term studies will be presented together with the present POPs strategy of the Czech government based on the conclusions of the National implementation plan of the Stockholm Convention on POPs.

Keywords: POP pesticides, Cetral European, regional background monitoring, integrated monitoring.

Introduction

A risk of irreversible changes in the terrestric and aquatic ecosystems as well as a danger of the global climate change caused by the environmental pollution was first recognized in early 1960s. However, detection of such changes in the natural environment at regional and global levels requires a coordinated monitoring effort based on the broad international cooperation.

The integrated monitoring has four specific objectives: to establish the cause-effect relationships; to derive scientifically defensible pollution control or resource management programs; to measure an environmental response to the control measures; and to provide early warnings of the new problems [10]. A monitoring strategy usually starts with identification of the sources and potential risks in order to generate the testable hypotheses. A set of parameters has to be carefully selected, a sampling design and analytical techniques specified, and data variability estimated. Once the sampling scheme is defined, simultaneous physical, chemical and biological measurements of various ecosystem compartments can be launched. These may include meteorology, precipitation, runoff, sediment and soil chemistries, descriptive measurements of air, water, soil, and biota, population and community inventories, and a full suite of biological factors. The same strategy was applied when the integrative monitoring program was first established in the Kosetice observatory, south Bohemia, which is a part of the EMEP network.

European Monitoring and Evaluation Programme (EMEP) was established with a main goal to provide the governments and subsidiary bodies under the Convention on Long Range Trans-boundary Air Pollution (CLRTAP, signed in 1979) with qualified scientific information supporting the development and evaluation of the international protocols on emission reductions negotiated within the Convention. The EMEP program was initially focused on the trans-boundary transport of acidification and eutrophication. Later its scope broadened to address a formation of surface ozone, and more recently it also covered the volatile organic compounds (VOCs), persistent organic compounds (POPs), and heavy metals. EMEP stations monitoring POPs are presented in Fig. 1. From all 15 stations, there were only 6 sites reporting POPs in both, air and deposition, in 2004. Kosetice observatory in the Czech Republic is the only site where POPs are also determined in other environmental matrices, such as surface waters, sediments, soils, mosses, and needles and realised POPs part of integrated monitoring programmes (Fig. 2).

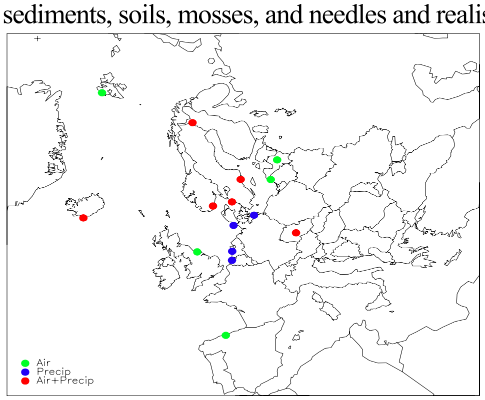


Fig. 1 POP monitoring EMEP network, 2000

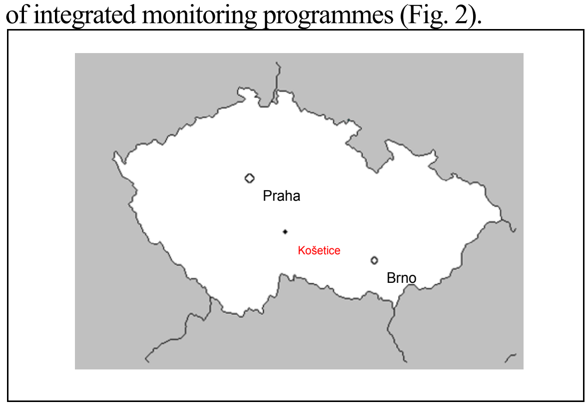


Fig. 2 Localization of the Kosetice observatory

POPs are a subclass of persistent, bioaccumulative, and toxic substances (PBTs), the organic chemicals likely to cause the adverse human health or environmental effects [2]. POPs are a group of compounds prone to the long-range atmospheric transport and deposition in the distant regions [3]. In 1992, a newly established initiative of United Nations Economic Commission for Europe in the UN-ECE region (Eastern and Western Europe, Canada, and USA) had prepared the Protocol on POPs (includes 16 POPs) with the goal to control, reduce or eliminate their discharges, emissions and losses. Beside that, a similar program of United Nations Environment Program (covering 12 POPs) was introduced in cooperation with the International Forum for Chemical Safety (UNEP/IFCS) [4]. Based on this, the Stockholm Convention was developed, signed and ratified 141 countries.

The objective of the Stockholm Convention on POPs can be stated to be as to protect human health and the environment from persistent organic pollutants by reducing or eliminating releases to the environment. Parties have agreed that they need a mechanism to measure whether this objective is reached. According to Article 16 of the Convention, its effectiveness shall be evaluated starting four years after the date of entry into force of the Convention and periodically thereafter at intervals to be decided by the Conference of the Parties (COP). For the global monitoring as a one part of effectiveness evaluation procedure, the Guidance on global monitoring Document was developed. The Guidance is focused on the development and implementation of arrangements to provide comparable monitoring information on the presence of the chemicals listed in Annexes A, B and C of the Convention, as well as their regional and global environmental transport.

The focus of the global programme to support the effectiveness evaluation of the Stockholm Convention is on environmental background concentrations in media with a high potential for comparability. The COP has decided that the air monitoring and human exposure through breast milk or blood serum will be used as core media for the first evaluation. For future evaluations, the COP has also decided to endeavour to supplement the core data with data from other media such as biota, water, soil, and sediments (SC-2/13). The present guidance is aimed at the core media for the first assessment and the document will be revised for future evaluations.

Integrated monitoring in the Czech Republic

A long-term project of integrated monitoring including both aquatic and terrestric environments has been carried out in the area of a background observatory of the Czech Hydrometeorological Institute in Kosetice, Czech Republic, since 1988 [5,6]. A small catchment of Anensky brook offers a diverse terrestrial ecosystem linked to the aquatic ecosystem of adjacent water bodies, and it includes all interacting components: atmosphere and depositions, plants and soils, brooks and ponds. While soils have more stable long term environmental memory related to contamination level, pattern, and distribution, sediments are more dynamic as they provide information on immediate situation within the watercourse.

Monitoring site

The Kosetice observatory of the Czech Hydrometeorological Institute (Fig. 2), located in the southern Czech Republic (N49°35´; E15°05´), was established as a regional station of the UNEP project of an integrated background monitoring network GEMS. The observations were launched in the late 1970s and the facility was completed in 1988.

Monitoring approach

POP monitoring in the Kosetice station is a part of the long-term cooperation between the Czech Hydrometeorological Institute and RECETOX, Masaryk University. It has been an important part of two RECETOX research projects – TOCOEN (Toxic Organic Compounds in the Environment, since 1988), and INCHEMIOL (Interactions among the chemicals, environment and biological systems and their conesquences on the global, regional and local scales, since 2005). A long-term integrated monitoring program carried on in the Kosetice background observatory in the Czech Republic was described in detail elsewhere [5,6].

Selection of compounds and matrices

Following set of compounds was recommended by EMEP for the initial phase of the measurements: polycyclic aromatic hydrocarbons (PAHs: benzo(a)pyrene), polychlorinated biphenyls (PCBs: IUPAC congeners number 28, 52, 101, 118, 153, 138, 180), hexachlorobenzene (HCB), α- and γ-chlordanes, α- and γ-hexachlorocyclohexanes (HCHs), p,p'-DDT, and p,p'-DDE. In Kosetice, a full set of US EPA 16 PAHs, seven indicator PCB congeners, p,p'-DDT, p,p'-DDD, and p,p'-DDE, α-, β-, γ-, δ-hexachlorocyclohexanes, hexachlorobenzene and pentachlorobenzene are being analyzed on the regular bases.

Results and discussion

Although the ambient air and wet deposition measurements have been carried on since 1988 in the Kosetice observatory, only POP data from the last ten years (1996-2005) were used for the evaluation of the long-term trends (Tab. 1). The main reason is a comparability of the results; the same sampling frequency as well as the same sampling and analytical techniques were employed during this period.

The measured concentrations of γ- HCHs were approximately two times higher than those of α-HCH, and the p,p'-DDE levels where almost a half order of magnitude higher than those of p,p'-DDT. Prevalence of DDT metabolites in the ambient air observed also in the samples of other environmental matrices from the Kosetice observatory [5-7] suggests that old burdens rather than a long-range transport are responsible for the levels of DDT compounds in the air.

A typical seasonality in the atmospheric POP pesticides concentrations can be seen in Figs. 3-5. Most of POPs pesticides were banned in Europe and their maxima are not connected to their production or seasonal application. They are present in the atmosphere due to their volatilization from the old deposits (soils, sediments, wastes) or possibly due to a long-range atmospheric transport from regions where they are still applied. In agreement with this hypothesis, elevated levels of chlorinated compounds can be observed during the summer when increasing temperatures enhance the evaporation of these chemicals from the old burdens.

POP pesticides concentrations, Kosetice observatory, minimum, maximum, mean and median air, wet deposition, surface water, sediment, soil, mosses and needles, Kosetice 1996-2005

Table 1

Matrix, Unit	Species	Mean	Median	Min	Max	Matrix, Unit	Species	Mean	Median	Min	Max
Air (PUF) [ng m^{-3}]	Σ HCHs	0.068	0.044	BQL	0.771	Sediment [ng g^{-1}]	Σ HCHs	0.47	0.27	BQL	4.09
	Σ DDTs	0.036	0.030	0.001	0.207		Σ DDTs	11.15	4.76	0,28	68.15
	HCB	0.145	0.115	BQL	0.831		HCB	3.26	0.39	0,04	78.08
Air (QF) [ng m^{-3}]	Σ HCHs	0.009	0.004	BQL	0.104	Soil [ng g^{-1}]	Σ HCHs	1.06	0.43	BQL	20.43
	Σ DDTs	0.004	0.003	BQL	0.050		Σ DDTs	20.47	5.12	BQL	193.97
	HCB	0.004	0.002	0.001	0.134		HCB	1.47	0.86	BQL	9.18
Rain water [ng L^{-1}]	Σ HCHs	32.300	5.200	BQL	2256.8	Mosses [ng g^{-1}]	Σ HCHs	4.55	0.89	BQL	150.54
	Σ DDTs	2.530	0.200	BQL	95.500		Σ DDTs	2.24	2.00	BQL	7.17
	HCB	0.137	0.050	BQL	2.500		HCB	2.73	0.76	BQL	47.26
Water [ng L^{-1}]	Σ HCHs	6.10	2.10	BQL	68.50	Needles [ng g^{-1}]	Σ HCHs	6.44	2.55	BQL	36.57
	Σ DDTs	1.15	0.20	BQL	14.20		Σ DDTs	4.21	2.70	BQL	25.16
	HCB	0.51	0.30	0,10	1.80		HCB	4.84	2.79	BQL	51.42

BQL = bellow quantification limit. Quantification limit is 1 pg m^{-3} for the individual compounds in the ambient air, 50 pg L^{-1} in the rain water, 10 pg g^{-1} for the individual compounds in the solid matrices, and 50 pg L^{-1} in the surface water.

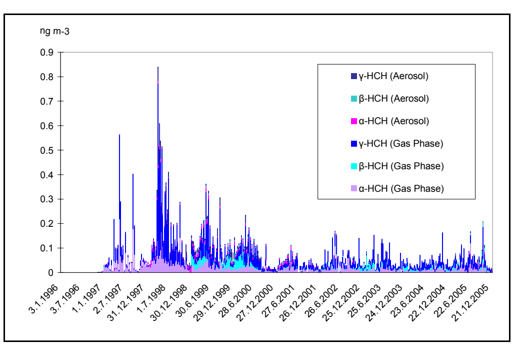


Figure 3: Σ HCHs in the ambient air, Kosetice observatory, 1996-2005

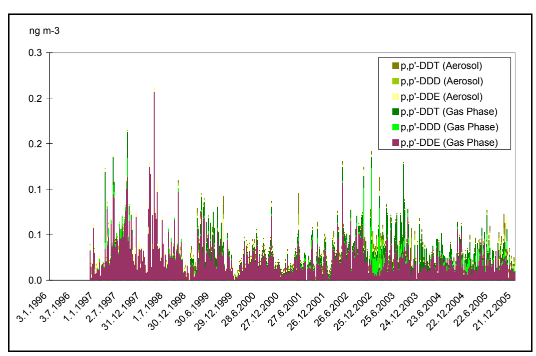


Figure 4: Σ DDTs in the ambient air, Kosetice observatory, 1996-2005

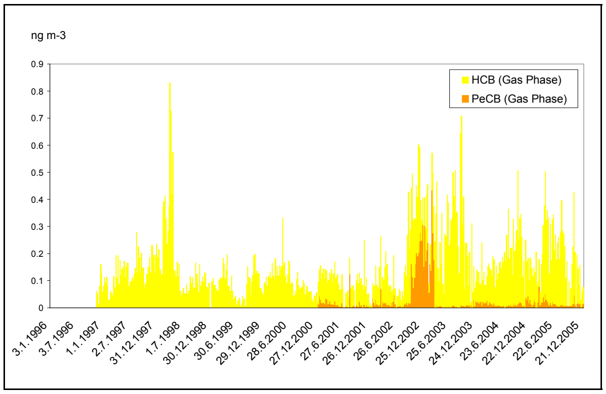


Figure 5. HCB and PeCB in the air, Kosetice observatory, 1996-2005

Rainwater POP concentrations reflect the air concentrations. γ-HCH was detected in highest concentrations from all chlorinated compounds. The mean concentration of chlorinated compounds were low - 5 ng L^{-1} for the sum of HCHs, 0.2 ng L^{-1} for the sum of DDT, DDD, and DDE, and 0.05 ng L^{-1} for HCB.

The annual median concentrations were calculated for all POP subgroups (PAHs, PCBs, DDTs, HCHs and HCB) in the air (gas and particulate phase) as well as in the rain ánd surface waters, sediments, soils, mosses and needles and resulting ten annual values for the period of 1996-2005 were compared to evaluate the long-term trends for each group of compounds and each matrix (Figs. 6a-i). The analysis revealed time related changes in the amounts of chemical species.

Interestingly, high summer maxima of OCPs were observed in 1997/8 and 2002/3 years. These fluctuations in the annual medians of OCPs (and PCBs too) may reflect the major flood events in the Czech Republic in 1997 and 2002. A large area of central and southern Moravia (to the east from Kosetice) was flooded in 1997, including the industrial and agricultural facilities where various chemicals were stored. The floods were followed by extremely hot summer therefore those chemicals could evaporate from impacted areas and be a subject of the atmospheric transport. Similarly, the central part of Bohemia (to the west from Kosetice, Prague included) was flooded in 2002. Several large chemical enterprises located to the north of Prague were severely damaged and variety of chemicals escaped to the surface waters and was distributed with the flood. According to the results of our previous research focused on the impact of these flood events on aquatic and terrestrial environments [9], one of the effects of floods is a re-distribution of the old burdens from the river sediments to the surface layers of the soils that were flooded. Semi-volatile persistent organic compounds can easily re-evaporate from these top soil levels during the warm season. This is probably the source of elevated atmospheric concentration of chlorinated POPs in the years following these disasters. The reason why the floods in 1997 so significantly affected the background levels of OCPs and PCBs, and the flood events in 2002 had much smaller impact, can be a character of the flooded regions. HCHs exhibited extremely high levels in the summer of 1998, and gradually decreased in 1999 and 2000 (Figs. 6a-i).

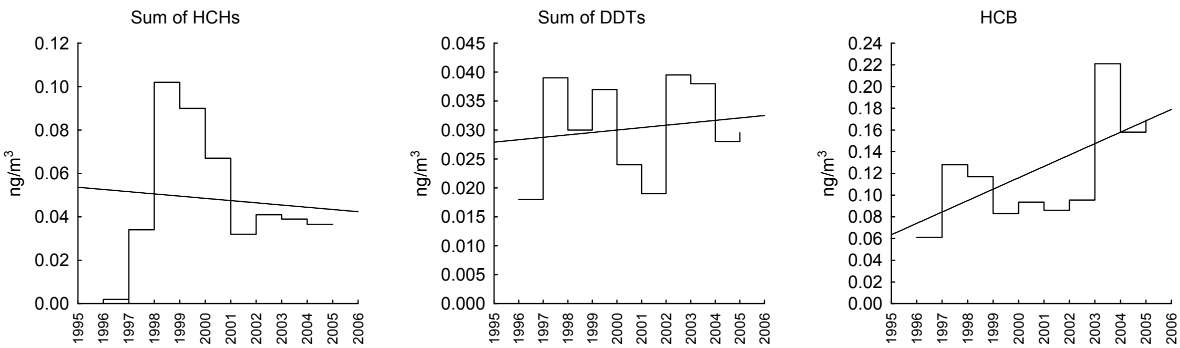
DDTs followed the same pattern of the very high summer maxima in 1997 and 1998 and the gradual decrease until 2001. However, since the second increase in 2002-2003, the concentrations of DDT and its metabolites have stabilized at the elevated levels. This is probably again connected to the flood events in 2002 when the chemical factories, former producers of pesticides, agricultural enterprises as well as the pesticide storage facilities were affected and the large amounts of pesticides escaped to the environment. However the influence of the local sources (evaporation from the soils or ponds) cannot be excluded. A new DDT fingerprint is typical with a less pronounced seasonal variability and the enhanced fraction of p,p'-DDD.

Hexachlorobenzene is the only analyte showing statistically significant increasing trend in the air concentrations. We can still detect high summer air concentrations of HCB following the floods in 1997 but – similarly to DDT – floods in 2002 seem to have more lasting impact. The very high concentrations from 2002 and 2003 have only declined very slowly in the next few years. Thus, what seems to be an increasing trend in the statistical analysis of annual medians is most probably only a very slow recovery of the ecosystem from the severe impact of the natural disaster. At the same time, an extreme level of pentachlorobenzene as a degradation product of HCB was detected in 2002.

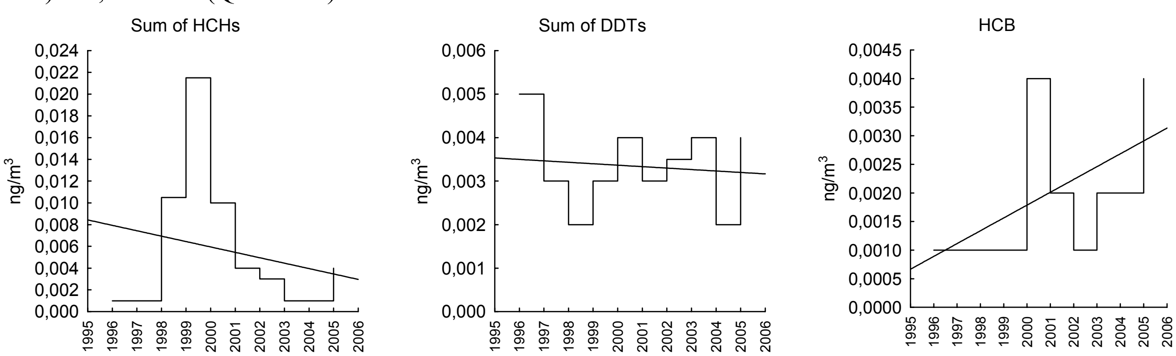
Minimum, maximum, mean and median levels of selected organic compounds found in various environmental matrices in the Kosetice station between 1996 and 2005 are listed in Table 1. Highest concentrations of POPs were found in soils and sediments, the levels in surface water were generally very low. The measured concentrations of γ- HCH were higher than those of α-HCH in all moss, needle, and soil samples, but in sediments, α-HCH occasionally prevailed. There were several soil and sediment samples with the significant fraction of β-HCH as well. The p,p'-DDE levels where higher than those of p,p'-DDT in most of the soil samples, however, there were the sampling sites (5 and 9) with p,p'-DDT dominating the pattern. In some sites (13), a significant change of the DDT/DDE ratio in the last ten years can be observed. On the contrary, p,p'-DDE dominated in all moss, needle, and sediment samples.

Figure 6a-i: Time related trends of POPs in environmental matrices, observatory Košetice, (PUF); the line represents estimated trend

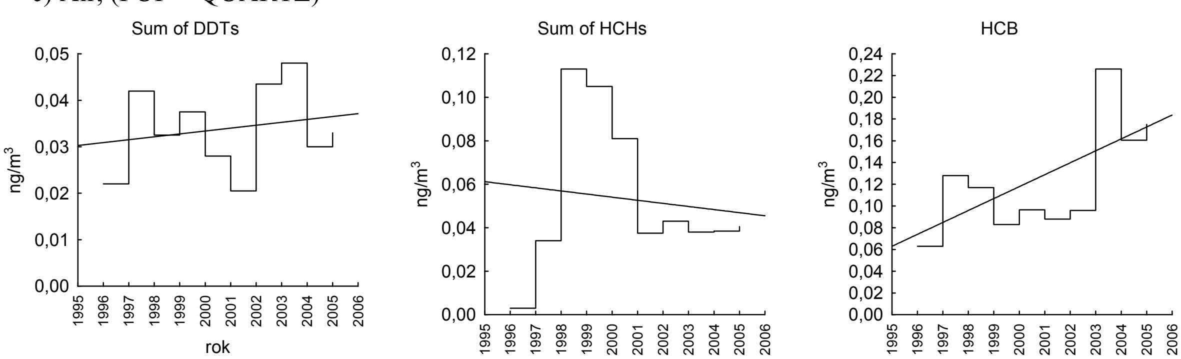
a) Air, Gas Phase



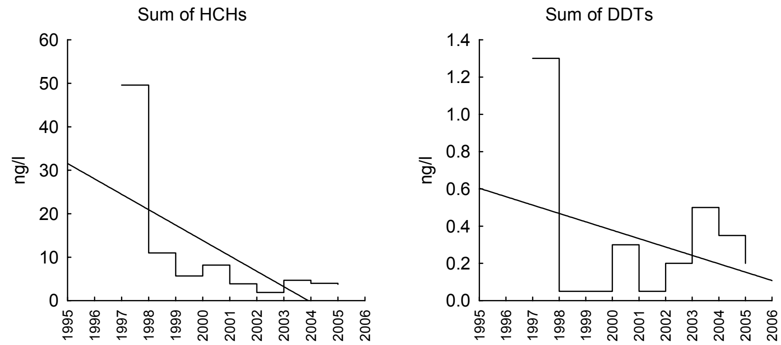
b) Air, Aerosol (QUARTZ)



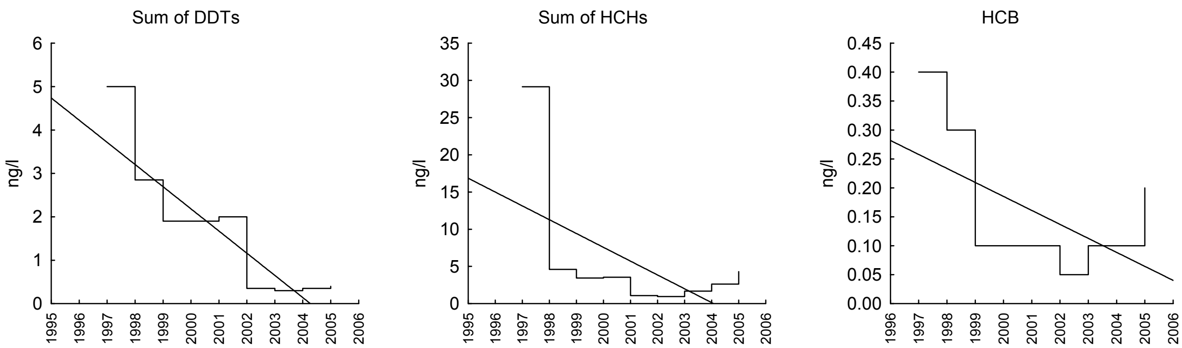
c) Air, (PUF + QUARTZ)



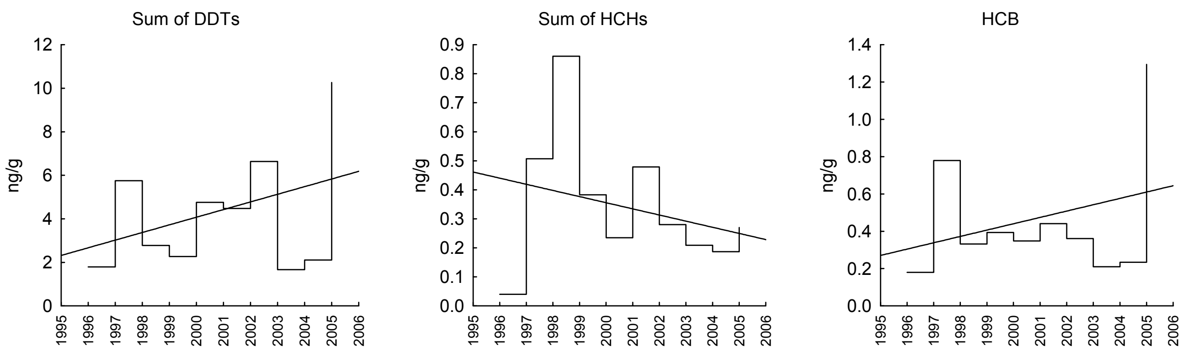
d) Rain water



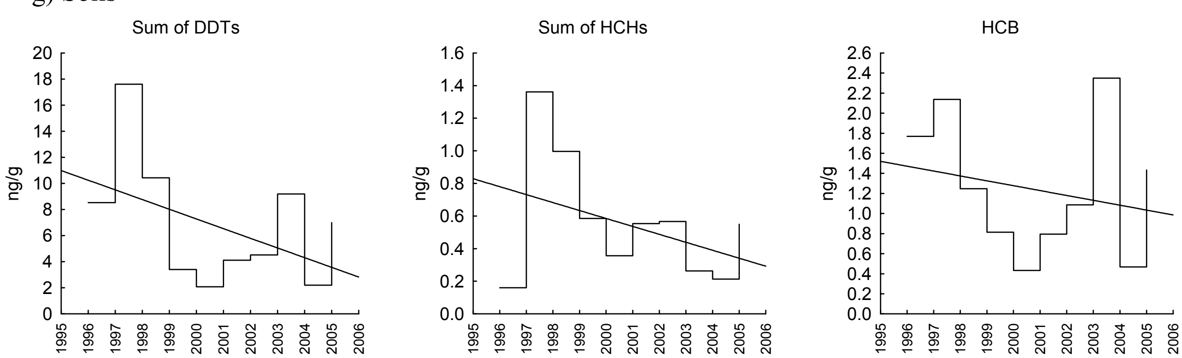
e) Surface waters



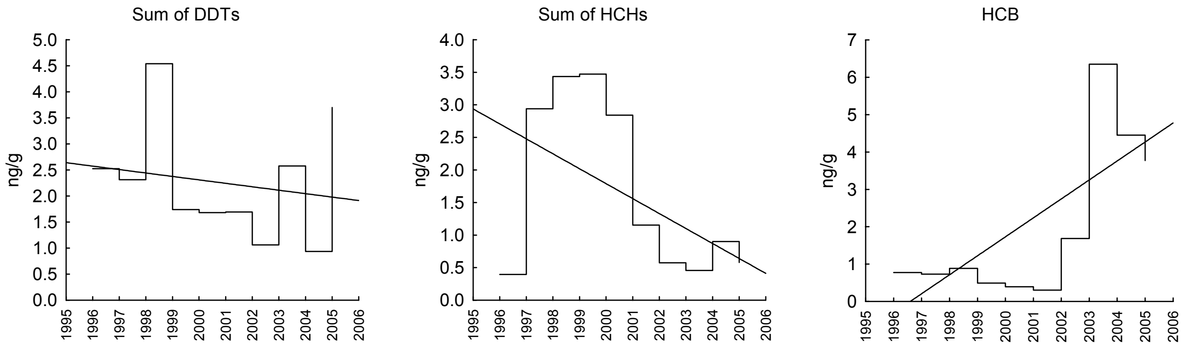
f) Sediments



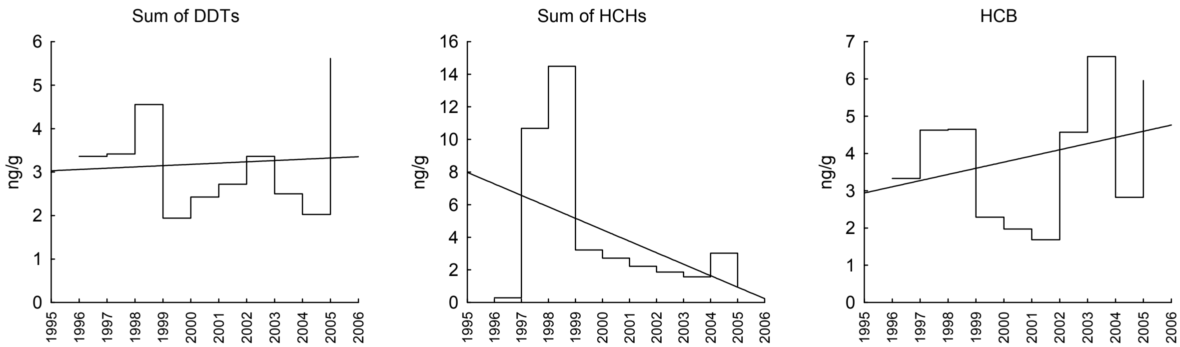
g) Soils



h) Mosses



i) Needles



Conclusions

Data from ten years of integrated monitoring in the Kosetice observatory were used in this project to assess the long-term trends in the European background levels of persistent organic pollutants in the ambient air and wet deposition. As can be seen from our results, most of the selected compounds exhibit decreasing trends in the last decade. This is consistent with data reported from other European sites.

Results of our project proved that the long-term background monitoring is not only an excellent way to study the regional levels and trends but also a powerful tool for evaluation of an impact of various local, regional or global events – from industrial accidents to natural disasters. As such, it has a crucial role in the effectiveness evaluation of various global measures and international conventions focused on persistent toxic substances, reduction of their emissions and environmental impacts.

The POP concentrations in sediment, surface water, soils, moss, and needle samples have been monitored in 16 sampling sites near the background observatory Kosetice over the period of eighteen years. There was a significant variability in occurrence and distribution of selected and OCPs are homogenous in time and space since they are more influenced by the diffusive sources such as an evaporation from contaminated soils. However even here we can detect the events with the high environmental impact (floods, industrial disasters, constructions) transporting significant amounts of persistent compounds from their primary sources, storage places or contaminated sites to the surface waters and soils where they are a subject of evaporation in the following years. The moss or needle samples precisely reflect a current contamination of the atmosphere, while the sediment and soil samples (especially the organic carbon rich forest soils which can act as an efficient sink of the POP pollution) provide us with the long-term record of the regional pollution. At the same time we need to be aware that the matrices with high accumulation potential can turn from the sinks to the local sources of POPs. Such complex background monitoring data can be used not only to evaluate the long-term trends in the environmental pollution or the impact of various short-term events. They are very valuable for the assessments of the fate of persistent compounds in the environment – their cycling between compartments, long-range transport or accumulation in various matrices – as well as for the validation of various distribution and transport models. Results of our project presented in this article strongly support the argument that the long-term monitoring programs are of the high importance for the decision making and legislation as well as for the effectiveness evaluation of various measures.

Acknowledgements

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References:

1. G.B. Wiersma, Environmental monitoring, CRC Press LLC, Boca Raton, New York, Washington D.C., 2004.
2. H.W. Wallack, D.J. Bakker, I.Brandt, E.Brostrom-Lundén, A.Brouwer, K.R. Bull, C.Gough, R.Guardans, I.Holoubek, B.Jansson, R.Koch, J.Kuylenstirna, A.Lecloux, D.Mackay, P.McCutcheon, P.Mocarelli and R.D.F. Taalman, Environmental Toxicology and Pharmacology, 1998, 6, 143-175.
3. UN-ECE: The Convention on Long-range Transboundary Air Pollution, 1998.
4. UNEP: Stockholm Convention on Persistent Organic Pollutants, 2001.
5. I.Holoubek, J.Klánová, J.Jarkovský, J.Kohoutek: Trends in background levels of persistent organic pollutants at Kosetice observatory, Czech Republic. Part I. Ambient air and wet deposition 1988-2005. J. Environ. Monitoring 9, 557 – 563 (2007).
6. I.Holoubek, J.Klánová, J.Jarkovský, V.Kubík, V.J. Helešic: Trends in background levels of persistent organic pollutants at Kosetice observatory, Czech Republic. Part II. Aquatic and terrestric environments 1988-2005. J. Environ. Monitoring, 9, 564 – 571 (2007).
7. I.Holoubek, A.Ansorgova, V.Shatalov, S.Dutchak and J.Kohoutek, Environ. Sci. Pollut. Res., 2001, 8, 201-211.
8. K.Hilscherova, L.Dusek, V.Kubik, J.Hofman, P.Cupr, J.Klanova, I.Holoubek: Redistribution of Organic Pollutants in River Sediments and Alluvial Soils Related to Major Floods. Journal of Soils and Sediments 7 (3), 167-177 (2007).

THE OBSOLETE PESTICIDES STOCKS AS POTENTIALLY STRONG SOURCE OF ENVIRONMENT POLLUTION

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In Ukraine the problem of management of obsolete pesticides (OP) requires an urgent decision, because about 20 000 t of these dangerous substances are distributed across the country. Research showed the presence of hazardous substances in the environment, including possible ingress into the food chain. Although in Ukraine legislation about toxic waste and recommendations on work with OP exist, the pace of funding and decision making remains unsatisfactory. In order to analyze the situation and develop new ways of problem solving, the group of specialists from highly regarded scientific establishments and related services of Ukraine jointly with United States Environmental Protection Agency executed a demonstration project under the name "Management and Destruction of Obsolete Pesticides in Pilot Oblasts in Ukraine (Cherkassy and Lviv Oblasts)".

Resulting from three years of work was identification of substances stored in 6 stockpiles of OP, and completion of re-packaging of these stocks. A total of 19.5 t of OP were disposed at specialized enterprise. The project also undertook research into maintenance of remaining amounts of pesticides and their vertical and horizontal migration in soils adjoining storage sites, research began on phytoremediation and microbial destruction in soils adjoining storage sites.

Keywords: obsolete pesticides, polluted soils, analytical methods, phytoremediation, microbial destruction, environment.

Introduction

According to FAO data, about 500 000 t of OP were accumulated in the world, including 20 000 t in Ukraine at the beginning of 2005. More than 2000 t belong to persistent organic pollutants (POPs) (Ligostaeva Y., Antonov A.). POPs belong to different chemical classes, but all of them are highly toxic, stable to decomposition, they can be carried at long distances by air and water, and they are accumulated in fatty tissue *(Stockholm convention)*.

In Ukraine the problem of management of OP requires an urgent decision, because about 20,000 t of these dangerous substances are distributed across the country. Ownership of many of such stocks has passed to farmers, and new proprietors frequently do not know what to do with such stocks, the level of danger associated with these substances, and some proprietors are poorly informed about the legislation related to these stocks. The primary purpose of the project was demonstration of the entire sequence of activities related to clean up of such stocks, following existing recommendations and within the framework of country legislation. Concomitant tasks included: a) conducting research linked with soil remediation, focused on the area adjoining obsolete pesticide storage sites; b) investigation of promising ecologically acceptable technologies of treatment/processing of obsolete pesticides.

Through proper storage and packing such pesticides can be rendered less harmful to human health and the environment. Research has shown the presence of hazardous substances in the environment, including possible ingress into the food chain. Ownership of many of such stocks has passed to farmers, and new proprietors frequently do not know what to do with such stocks, the level of danger associated with these substances, and some proprietors are poorly informed about the legislation related to these stocks. Despite national legislation and regulations, which include five (5) Laws, the problem of OP remains less than properly addressed, and the pace of funding and decision making remains unsatisfactory.

The partner project with US Environmental Protection Agency (EPA USA) began in the Ukrainian Laboratory of Quality and Safety of Agricultural Products of the National Agricultural University in August, 2004. Complicated research into the problem brought in a number of institutes of NAS of Ukraine and specialists working at the Ministry of Environmental Protection of Ukraine. Six (6) locations of pilot research projects were selected: 3 storage sites in Zhydachiv district of the L'vov area (V.Grusiyatichi, V.Kniselo and V.Bakivtsi) and 3 storage sites in the Korsun'-Shevchenkiv district of the Cherkassy area (V.Kvitki, V.Petrushki and V.Komarivka). The purpose of this article is an attempt to present part of our information about project implementation, in particular the main analytical question of determining the residue amounts of multicomponent mixtures of persistent pesticides in soils, adjoining the places of storage of obsolete pesticides, to describe the method which was elaborated at our Laboratory and to inform in brief about other studies and activities.

Results and Discussion.

Our project was aimed at describing the entire work chain based on existing legislation, from the time of first entering the sites to the complete clean up of OP stocks. Based on obtained experience we had planned to discover the gaps in existing rules and to develop recommendations to improve management and disposal of OP pesticides, including how to prevent accumulation of OP and empty packing in rural areas of Ukraine in the future. The last official inventory data (Table 1) showed that non-identified pesticides was the main group of OP stocks.

Summarized Table from Official Inventory Data on 3 OP Stocks in Cherkassy oblast and 3 OP Stocks in L'viv oblast.

Table 1

Group	Cherkassy oblast L'viv oblast
Forbidden	1, 01 t 0,08 t
Obsolete	0,6 t 5,003 t
Non-identified	**14,661 t 1,775 t**

Before we started OP disposal, we performed some analyses to identify the substances in the stocks. It was to provide appropriate safety for workers and for the purpose of giving a more precise definition for monitoring of contaminants in soil and water.

Short list of the main results for the Project P-169 activity during the period of 3 years:

- Identification of substances, that are located at the 3 OP stocks in Lviv region and at the 3

OP stocks in Cherkassy region, was conducted; selected samples were analyzed by the nuclear magnet resonance method (NMR), infra-red spectroscopy (IRS), thin-layer chromatography, gas chromatography and high performance liquid chromatography (HPLC); research was conducted at the Ukrainian Laboratory of Quality and Safety of Agricultural Products (chromatography methods) and in the Institute of the Organic Chemistry of the NAS of Ukraine (NMR and IRS);

- During the project implementation (August 2004 - August 2007) we conducted some analysis to determine the operating substances, element analysis, pesticide residue quantities in different matrixes, monitoring of the pesticide residues in soil and plants during the process of remediation; there were 200 samples analyzed by the NMR method, 126 samples analyzed by the IRS method, 1591 samples analyzed by different chromatography methods and 77 other analyses (phytotoxicity and others);
- "List of agro chemicals and obsolete pesticide residues, found during inventory of the pilot stocks in Lviv and Cherkassy regions " and list of chemical Spectra was created;
- Repacking of OP, their transportation and destruction at the specialized enterprise (6,0 t from Lviv region and 13,5 t from Cherkassy region) were conducted;
- Stabilization of the OP conservation areas was conducted;
- With the aim of cost calculation of stock stabilization for owners we conducted financial estimation of the work chain, that should be conducted to clean up stocks;
- Some defects in legislation base were found; correction of these defects will help in updating and speeding up the work in this sphere;
- First results of territory remediation, that is around OP stocks, were obtained; character of soil contamination around OP stocks was determined; it was determined, that in Lviv region (Grusiyatichi village, Zhydachiv district) there is a domination of contamination by chlorine organic pesticides (COP), and in Cherkassy region (Kvitky village, Korsun-Shevchenkivskij district) – by COP, treflan, propiconazole and chlorpyriphos;
- Specific group of problems was determined, these problems are connected with OP;

- problem and need to be solved (destruction of counterfeit unregistered preparations, packages and so on.);
- Lessons aimed at formation of the ecologically-oriented outlook of pupils that reside in the territories of the project implementation was conducted;
- Scientific research in the field of organic and non-organic chemistry, ecology, analytical chemistry of xenobiotics was started.

Pictures of the OP stock in v. Kvitky, Cherkassy region before and after are presented in Images 1 and 2.

Image 1. OP warehouse condition before project, v. Kvitky, Cherkassy oblast, 2004

Image 2. The same OP warehouse after disposal, 2006

Special attention was devoted to analytical methods. We used mainly the methods already approved, but a lot of time was focused on improving this method. One of the problems connecting with obsolete pesticides stocks is pollution of adjacent soils. The contamination of soil and groundwater with different pesticides, mainly forbidden nowadays, has caused serious environmental problems. Analytical team from Ukrainian Laboratory of Quality and Safety of Agricultural Products has carried out a series of studies of pesticide residues in the soils, adjacent to obsolete pesticides stocks by using GLC/FID, GLC/ECD, GLC/MS methods.

Multiresidue methods of analyzing the pesticides are the most acceptable to the aims of monitoring and are established in many countries. In particular, the methods of determination of 29 chlorine-organic pesticides (COP) in drinking water are well known *(Official Methods of analysis of A.O.A.C.)*. Another well known method is the method for determining of 44 pesticides from the groups of organophosphorus pesticides (FOS) and COP in water, and complex of toxicants, containing a residue of 91 pesticides, in fruit and vegetables. In connection with wide distribution of methods of GLC/MS and LC/MS in combination with solid state extraction the examined methods of analysis were improved (*Becker G., Official Methods of analysis of A.O.A.C.)*.

In Ukraine at different times the prototypes of modern methods for determining of multiresidue methods were developed in one sample (*Klissenko et al*), although the principles of development differs a little from that presented above. In our work the method for determining of 20 persistent pesticides is accomplished in one test of soil. It is based on extraction of a complex of pesticides from the sample of soil by introduction of acetone and by shaking and subsequent filtration, to clean up through redistribution in the binary system: water acetone - n- hexane, concentration of extracts and determination of capillary gas chromatography a method with selective detectors: TID and ECD. To increase the reliability of identification of micro quantities of the analyzed pesticides in accordance with the principles of quality of the analytical measuring management, capillary GLC/MS was used with an ionic trap. Details of methods and terms of chromatography are described in separate article in Ukrainian Journal of Chromatography Society (#3, 2005) The developed method is simple on execution, allows improved savings in solvents, can be reproduced quickly (duration of analysis does not exceed 4 hours, but by using the more rapid methods of extraction, is accomplished in less time). As an example, in the Table 2 below are shown the results of the application of the multiresidue method for pesticides in the soils, selected on the territories adjoining obsolete pesticides stocks. Soils were selected in the different areas of Ukraine. In view of the length of time in storage for many pesticides in these facilities, the high level of adjacent soil contamination does not cause a surprise, but requires giving the fact of the extraordinary value.

Pesticides residue in soils adjacent to obsolete pesticide stocks

Table 2

Pesticides residue, mg/kg	**L'viv oblast, v. Grusiyatichi**		**Cherkassy oblast, v. Kvitky**	
	Distance from the stock		**Distance from the stock**	
	1-3 m	**20 m**	**1-3 m**	**20 m**
α-HCH	nd	0,01	0,04	nd
β-HCH	0,25	0,44	4,24	0,28
γ-HCH	0,05	0,26	0,03	0,03
treflan	nd	nd	113,0	nd
simazine	nd	nd	nd	nd
atrazine	nd	nd	31,82	0,10
propazine	nd	nd	nd	nd
promethrine	nd	nd	nd	nd
dimethoate	0,01	nd	0,28	0,01
diazinone	0,07	nd	0,05	0,01
parathion-methyl	nd	nd	nd	nd
malation	0,01	nd	nd	nd
aldrine	nd	nd	nd	0,01
heptachore	nd	nd	nd	nd
pendimethaline	nd	nd	nd	nd
DDD	0,01	nd	0,06	0,10
DDE	0,18	0,01	0,11	2,67
DDT	0,15	0,01	0,28	0,32
phosalone	nd	nd	nd	nd

Nd – non detected

Data analysis for Table 3 shows that residue of COP (β, γ - HCH, DDT and DDE), treflan and atrazine considerably exceed MAC.

Another aspect of project activity was to push phytoremediation and biodegradation study. Before we started that study, we investigated levels of pollution in the soils, and had studied the vertical and horizontal mobility of OP in adjacent soils (Image 3), level of pesticides in grass (Image 4).

Image 3. Fate in soil: vertical mobility adjacent soil (Grusiyatichi village, L'viv region)

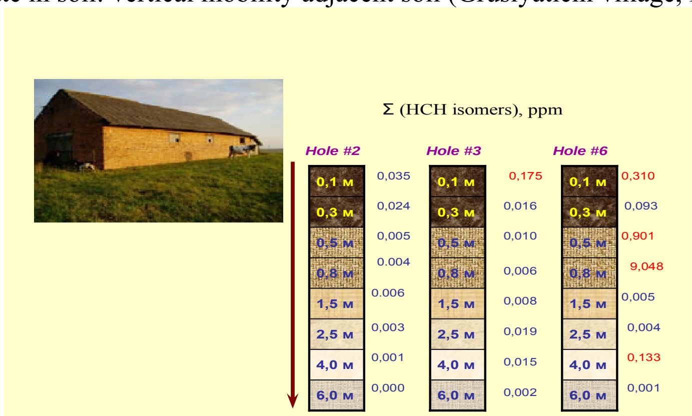

Image 4.

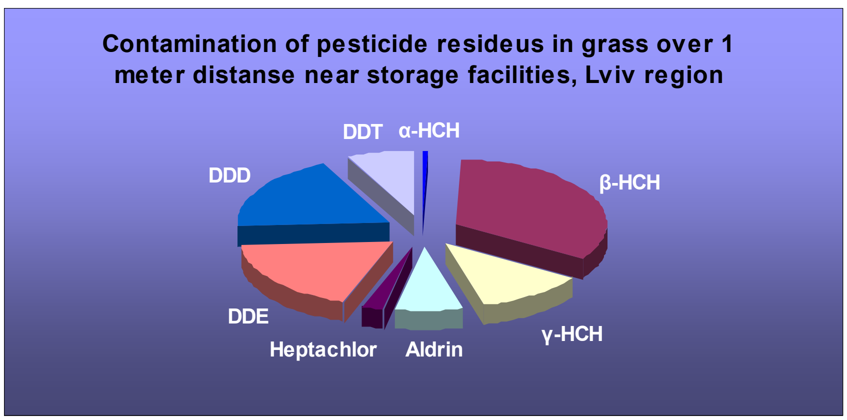

Image 5. Plots for phytoremedion preliminary study in v.Grusiyatychy, L'viv oblast, 2006.

Preliminary bioaccumulation study of OP in plants from different species (*Poaceae, Fabaceae, Brassicaceae, Amarantaceae, Piperaceae* etc.) was conducted. Some species were deleted from following study because of low level of adaptive ability to strong soil pollution. We are in process of field and laboratory study of bioaccumulation and biodegradation.

Within the framework we also devoted attention to risk communication aspects, in particular, the informative lessons were conducted for schoolchildren about the necessity of careful attitude toward the environment and safety during work with household chemical goods. It is necessary to pay special attention to forming an ecologically directed world view for schoolchildren and to conduct teaching on the rules of safety during work with pesticides on the homestead land for adults.

During the 3 year period of project activities more than 20 articles (scientific and in mass media) were published, interviews were given on TV, presentations at the international and Ukrainian conferences and round tables were made. Positive regards to the project were made during discussions of the conducted works in the Department of Chemical Substances Safety of the Ministry of Environmental Protection of Ukraine (September, 2005), which is the Department responsible for pesticide registration.

At several meetings of project participants, which were conducted with specialists of the Ministry of Environmental Protection of Ukraine, specialists and experts from different institutions for the purpose of discussion about project results, a number of conclusions were made:

- One approach to small OP stocks management and stabilization of OP storage locations was demonstrated;
- Significant scientific work on organic chemistry, analytical chemistry, ecotoxicology, general biology, was conducted;
- Contribution to the development of a new direction- ecological management of the anthropogenic activity-was made
- Solutions to separate organizational questions were offered [proposals on updating needed infrastructure; information about cost of works complex (on the example of works for clean up of 6 stocks) and propositions on possible additional financing resources];
- Complex works on prediscovery remediation and biodegradation study of the contaminated territories in 2 climatic zones was done;
- Need for significant development of lesson plans for children including safety precautions around stocks and informing mass media, was determined.

Practical work showed the necessity of improving legislation in the area of management, in development of scientific research, in storage of obsolete pesticides, on the subject of remediation of polluted territories, to strengthen monitoring programs and analytical methods of research and to create the proper infrastructure for management of waste.

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References:

1. Becker G. Organohalohen, Organophosphorus and Triazine Compounds, S 8, German ver. – 1985, S8, p.2-8.
2. Klissenko et al: Аналітична хімія залишкових кількостей пестицидів.–К.,1999. -238 с.
3. Ligostaeva Ye.V., Antonov A.V. Analysis of the Current Status of Treatment of Prohibited and Obsolete Pesticides in the Context of the Development of the National Plan for Implementation of the Stokholm Convention on POPs. – Abstracts, 8th International HCH and Pesticides Forum, 26-28 May, 2005, Sophia, Bulgaria – p.22-23.
4. (Stockholm Convention) : Стокгольмська конвенція про стійкі органічні забруднювачі. – Офіційний переклад на українську мову. Затверджено Правовим департаментом МЗС України . – Вид. СПД „Вальд", К., 2004 – 47 с.
5. Official Methods of analysis of A.O.A.C. International, ed. P. Gunnif ,16 ed., 1999, Maryland , USA, v.1, ch.10,

p.13-17, 26-31.

6. Official Methods of analysis of A.O.A.C. International, ed. W. Horwitz ,18 ed., 2005, Maryland , USA, v.1, ch.10.p.10-17.
7. Определение множественных остатков пестицидов в почвах прискладских территорий - С.Д. Мельничук, В.И. Лоханская, Ю.С. Баранов, В.И. Цвилиховский, О.В. Земцова, Е.В. Жук - 2005 - Журнал хроматографічного товариства – т.М- № 3, стор. 4-10 УДК 543.544.3 ; ISSN 1729-7192.

METHODOLOGY OF THE DERIVATION OF PRECAUTIONARY SOIL VALUES FOR HCH AND TRIGGER VALUES FOR THE PATHWAY SOIL-PLANT ACCORDING TO THE GERMAN SOIL PROTECTION REGULATIONS

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According to the German Federal Soil Protection Act the natural function of soil as a habitat for human beings, animals, plants and soil organisms as well as the production function is among others to be protected by deriving soil values for important chemicals regarding their amounts in the environment, their persistence and/or their toxicity.

So the Federal Soil Protection Act of 1998 and its Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) of July 12th, 1999 contain precautionary values and trigger values for the protection of soil functions. For both criteria there are values for HCH whose derivation is explained.

Trigger values are related to various soil uses and objectives of protection, which are „human health“, „quality of food and feed“, and „leachate to groundwater“. Any procedure to derive trigger values for the objective „quality of food and feed“ has to consider the soil-plant transfer of chemicals for soils under agricultural use and household gardens. Thus, the production function of soil is taken into account.

For precautionary values especially the habitat function of soil for micro- and macroorganisms plays an important role because reduction and transformation processes in soil are a common performance of soil organisms as well as chemical and physical soil properties – 80 % of substantial transformation processes in soil are related to soil flora and fauna.

A final recommendation for legally binding soil values includes a plausibility check of the mathematically derived values as well as with natural background concentrations, soil values for other pathways and soil values used in legislation of other countries, which will be discussed.

Key words: Soil-plant transfer of organic substances, precaution levels, trigger levels, action levels, HCH.

Introduction

The Federal Soil Protection Act (Anonymus, 1998) was put into practice by the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) of July 12th, 1999 (Anonymus, 1999a). Precautionary values and trigger values as laid down in the Law are an important instrument to realise its requirements.

"Precaution levels" are indicating a certain chance of future oil problems which need to be addressed in order to avert upcoming damages.

“Trigger values” are triggering further investigations to ascertain (verify/falsify) whether a contamination implies a danger.

“Action levels" are generally indicating a danger which has to be warded off; further investigations to ascertain the danger are usually not necessary.

It is within the scope of the publication to give a summary on the methodology and results of precaution and trigger value derivation with respect to the soil-plant transfer process especially for HCH used very intensively as pesticide in the past in the some countries still today.

Derivation of precautionary soil values

According to the German Federal Soil Protection Act the natural function of soil as a habitat for human beings, animals, plants and soil organisms is among others to be protected against any disruption.

To maintain precaution against negative impacts precautionary soil values for important chemicals regarding their amounts in the environment, their persistence and their toxicity were derived.

§ 8 Federal Soil Protection Act defines precautionary soil values as **“….soil values which, if exceeded, shall normally mean there is reason that concern for a harmful soil change exists, taking geogenic or wide-spread, settlement-related pollutant concentrations into account… .”**

Methodology

Parameters considered for the derivation of precautionary values in the Federal Soil Protection and Contaminated Sites Ordinance of 1999 were the following:

1) Data on the accumulation and **effect of pollutants** in soils provided the basis for establishing precautionary values. Reference was made, first of all, to the variety of data given in literature on **ecotoxicological effect thresholds** (habitat, buffer, degradation and sink function for substance caused effects). Ecological effect thresholds for heavy metals, PCB and PAH were derived on the basis of direct assessment of data on No-Effect Level. To this end, the variation range given in literature as to the low/lowest NOECs and LOECs for individual species was used. It has to be mentioned in particular that especially for heavy metals partly drastically increased soil concentrations as compared to NOECs and LOECs are given in literature, which, however, should be seen in the context of the proposed aim of investigation.

If possible, the effect of soil pollutants on other targets to be protected (e.g. food plants including phytotoxic effects, groundwater and human health) was evaluated in addition.

2) For heavy metals the effect thresholds determined were checked against **soil background values** in order to pay regard to the soil as **integral part of the ecosystem**.

For organic pollutants no background values because they should not accumulate at all in the environment.

3) The sensibility of soils was taken into consideration by **classification of the soil texture** (clay, loam, sand) and by using the pH-value for heavy metals. Soils with significantly increased background contents are evaluated separately.

For organic substances not the pH-value but rather the humus content of soils is decisive for the mobilization or immobilization of substances. The differentiation of humus contents required for precautionary values was chosen in such a way that it corresponds to the different forms of cultivation. This requirement was fulfilled by the distinction in "greater than or less than 8 %".

For precautionary values especially the habitat function of soil for micro- and macroorganisms plays an important role because reduction and transformation processes in soil are a common performance of soil organisms as well as chemical and physical soil properties – 80 % of substantial transformation processes in soil are related to soil flora and fauna (Terytze und Vogel 2007).

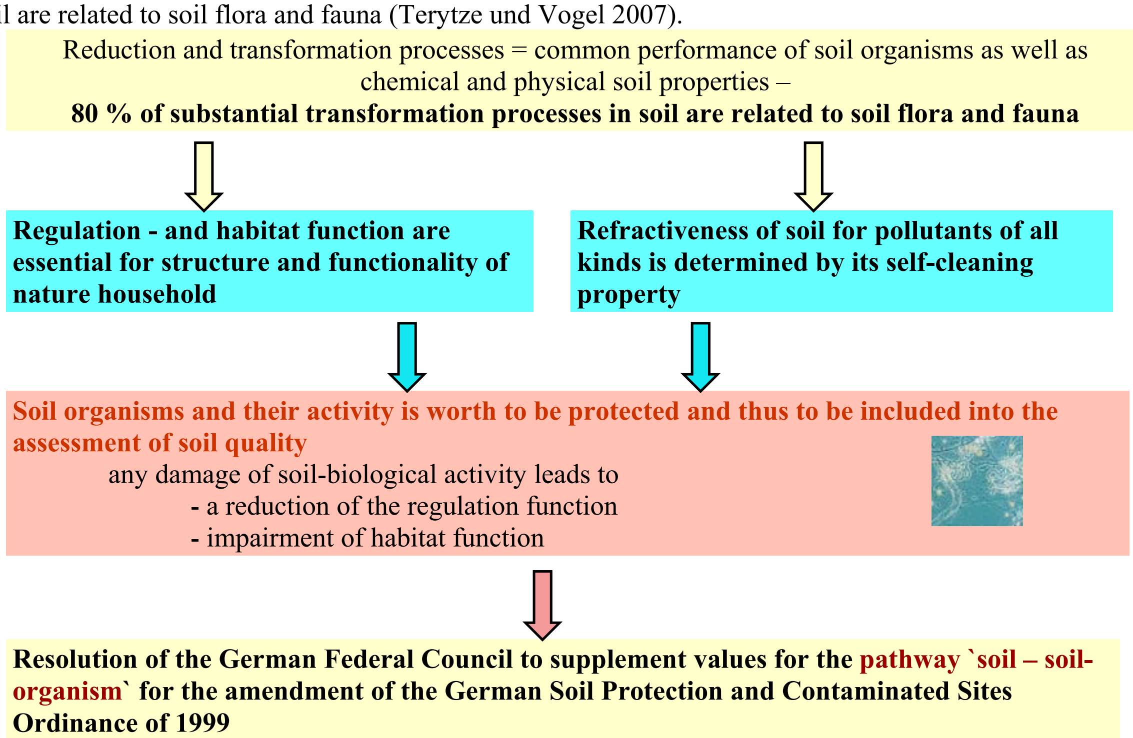

Figure 1: Importance of soil flora and fauna

For the current **amendment of the German Soil Protection and Contaminated Sites Ordinance** of 1999 already **existing precautionary values were checked against extrapolated EC_{10}/NOEC-values** based on various effect data concerning microbial activity, effects on soil animals and plant interference that were collected and entered into the 'SoilValue' database of the German Federal Environment Agency. Additional precautionary values for further priority pollutants were defined this way (Römbke 2007).

The derivation of soil values was performed using the extrapolation model (**DIBAEX**) based on **"Species Sensitivity Distribution"** including various data of soil macro- and microorganisms and plants.

According to this methodology soil ecosystem is considered to be protected if 95% of all species feature an EC_{10} higher than the determined soil value of HC_5 (Wilke et al. 2003) as illustrated in the figure 2 below.

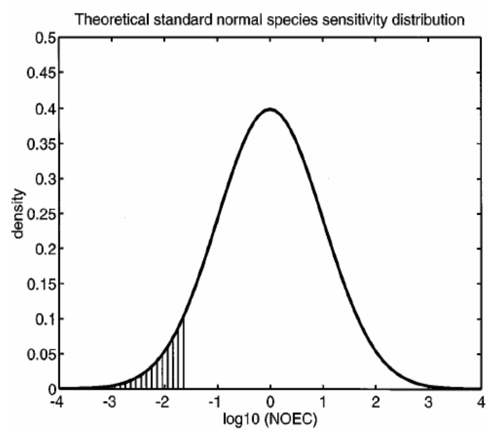

Figure 2: Theoretical standard normal species sensitivity distribution according to Aldenberg & Jaworska 2000)

Derivation of a precautionary soil value for HCH

For the derivation of a precautionary soil value for HCH the following microbial function data (4) and soil animals (3) were considered:

Ecotoxicological effect data for HCH (Römbke et al. 2007)

Table 1

Parameter	Median NOEC/EC_{10}	Number NOEC/EC_{10} [mg/kg]	log (NOEC/EC_{10})
ATP-content	2	1	0,301
CO_2-release	0,118	1	-0,928
Proteolytic activity	0,118	1	-0,928
Cellulose destruction	0,118	1	-0,928
Eisenia fetida/andrei	10	13	1,000
Enchytraeus albidus	11,245	2	1,051
Folsomia candida	0,0366	4	-1,437
Extrapolated value for the protection of 95% of all included organisms	**HC_5 = 0,1**		

On the basis of this data an extrapolated value for the protection of 95% of all included organisms of 0,1 mg/ kg was determinated with DIBAEX.

Considering different soil conditions for soils with low humus content a precautionary value of 0,1 mg/kg dm was determined, for soils with high humus content 0,5 mg/kg dm.

Derivation of trigger values

Trigger values are related to various soil uses and objectives of protection, which are „human health", „quality of food and feed", and „leachate to groundwater". Any procedure to derive trigger values for the objective „quality of food and feed" has to consider the soil-plant transfer of chemicals for soils under agricultural use and household gardens. Thus, the production function of soil is taken into account.

The exact procedure to obtain trigger values for „quality of food and feed" is laid down in the Federal Bulletin No. 161a (Anonymus, 1999b) and has to be followed when deriving justifiable values:

- Determination of the highest permissible pollutant concentrations in plants (preparation of the plant-oriented assessment standard),
- Description of substance transfer from the soil into plants, followed by calculatory derivation of the highest soil concentration that will still ensure compliance with the highest permissible plant concentration,
- Checking of the calculated soil values for plausibility, including estimation of the toxicological load from vegetables growing in gardens polluted with organic or mineral substances,
- Definition of trigger values.

By this means, trigger values for „quality of food and feed" already were derived for some metal compounds, namely arsenic, lead, cadmium, mercury and thallium. Beside metal compounds several organic substances are also of priority. So far, a trigger value was defined for benzo(a)pyrene.

Furthermore soil trigger values for the following substances are necessary: HCB, DDT, HCH. They are considered to be added to the Federal Soil Protection and Contaminated Sites Ordinance at the first amendment of the ordinance taking place this time.

It is within the scope of the presentation to give a summary on the methodology and results of precaution and trigger value derivation with respect to the soil-plant transfer process especially for HCH used as pesticide for a long time.

Database

Various research projects were conducted to derive trigger values for priority organic pollutants in the soil-plant pathway.

Due to a lack of data resources for the deriving of trigger values, a study framework first had to be developed to gather empirical data. The result is **TRANSFER**, a database using data from joint German Federal States research programmes and other data holdings at the Federal Environment Agency. The database allows soil concentrations of both inorganic and organic pollutants to be matched up with plant concentrations on the same site, and forms part of BIS, the national soil information system.

The Transfer database combines and integrates stocks of data that were managed separately in national and Federal States repositories in former times. Efficient data exchange at both Federal States and federal level became possible by new data compatibility standards. This aids the uniform enforcement of soil protection law. Data resources had also been set up to update and amend substance classifications and the precautionary, trigger and action values laid down in the Federal Soil Protection and Contaminated Sites Ordinance.

Methodology

a) Objective of protection: quality of food

1. Step: Consideration of maximum residue levels in/on plants

Trigger values are calculated by inclusion of maximum residue levels (MRL-levels, „Rückstandshöchstmengenverordnung" of 21.10.1999, modified on 20.11.2000) and ADI-values, respectively. In case these official values have not been derived for the compound under consideration a preliminary MRL´-value is assessed using N(L)OAEL-values and additionally applying a safety factor ($SF_{toxicological\ reference}$). In case none of the toxicologically relevant data is available the soil trigger value cannot be derived.

2. Step: Quantitative description of soil-plant transfer and derivation of a maximum acceptable soil content

The soil-plant transfer coefficient is defined as the quotient of the substance content in the respective plant compartment (given in dry weight) and the soil content (also given in dry weight):

$$f_{transfer\ (i)} = \frac{C_{plant\ (i)}\ [\text{mg/kg dm}]}{C_{soil}\ [\text{mg/kg dm}]}$$

Since the soil-plant transfer depends on both, soil and plant properties, ideally each food item and all representative soils should be tested. However, such a broad variety of experimental studies is not achievable and thus, the following assumptions and definitions were applied:

- The ideal data set is characterized by five soils and ten representative food items. As long as a heterogeneous data base is available with information, which is difficult to interpret, the five soils / ten food items data base is considered to be the optimum. In case systematic studies are published, a data set characterized by three soils and six food items is considered to be sufficient.

- In case the optimal soil data set is not available a safety factor (SF_{soil}) is applied to the mean transfer coefficient for each food item.

- The experimentally determined transfer coefficients for the individual food items each are combined and a mean is calculated.

The maximum tolerable soil content is, in a first step, calculated separately for each tested food item by using one of the alternative equations depending on the availability of MRL- and ADI-value, respectively.

In case MRL-values are available the equation is:

$$\text{max. tolerable soil content (i) [mg/kg dm]} = \frac{\text{HF x MRL (i) [mg/kg ww]}}{f_{\text{transfer (i)}}\ [1 - (\text{water content [\%] / 1oo})]}$$

with:

i = vegetable food (i)

MRL = maximum residue level [mg/kg wet weight]

$f_{transfer(i)}$ = mean of transfer coefficients for food item (i)

HF = hazard factor according to approach “toxicological hazard assessment of chemicals” (Anonymus, 1999c)

In case no MRL-value is available the equation is:

$$\text{max. tolerable soil content (i) [mg/kg dm]} = \frac{\text{HF x MRL´ (i) [mg/kg ww]}}{f_{\text{transfer (i)}}\ [1 - (\text{water content [\%] / 1oo})]}$$

where MRL´ is:

$$\text{MRL´ (i) [mg/kg]} = \frac{\text{ADI [mg/kg bw d] x 20 kg x portion (i) in food basket}}{\text{daily intake (i) [mg/kg]}}$$

with:

ADI = acceptable daily intake,

20 kg = reference for daily intake: girl, 4-6 years of age, sensitive subgroup, weight 20 kg.

The finally proposed maximum tolerable soil content, which is the basis for a plausibility check and expert-judgment, is identical with the lowest value out of the ensemble of calculated maximum tolerable soil contents for the individual food items. In case not all of the ten food items have been tested, again safety factors ($SF_{food\ item}$) are applied.

The finally proposed maximum tolerable soil content is multiplied with a so called „hazard factor“ (HF). Maximum residue levels are derived as precautionary values. Food with residues below these levels should not cause adverse health effects for all population groups including sensitive subgroups such as children. However, a maximum tolerable soil content – in the sense of a trigger value – does not reflect the precautionary principle but the avoidance of hazard to human health. Thus, a hazard factor is added. The use of such a „hazard factor“ is in accordance with the derivation of soil trigger values for the objective of protection „human health, direct soil contact“ as published in the Federal Bulletin No. 161a.

3 Step: Plausibility check *and*

4 Step: Final stipulation of trigger values.

The finally calculated maximum tolerable soil content has been multiplied with appropriate safety factors and the hazard factor is subjected to a plausibility check. The check comprises – among others – a comparison with background values and precautionary values in order to make the trigger values operable. Finally, the suggested triggers are stipulated in the course of a moderated round table discussion including expert-judgement.

b) Objective of protection: quality of feed

For the derivation of maximum tolerable soil contents for the objective of protection „quality of feed" the procedure as laid down in the Federal Bulletin No. 161a is followed:

- Grassland and soil under agricultural use (for maize) are treated identically.
- The legal basis for maximum tolerable plant levels is Directive (29/99/EEC) as well as the German „Futtermittelverordnung"
- The Directive (29/99/EEC) gives maximum tolerable plant levels for Aldrin, DDT, HCB, HCHs and Dioxins without differentiating between feed items.
- For other than these compounds or compound groups the maximum tolerable soil content currently cannot be derived (Terytze et al. 2007).

Derivation of the maximum tolerable soil content for HCH – trigger value for the pathway soil-plant.

Data availability for soil-plant uptake of HCH:

- data set on small scale laboratory studies and field studies are available
- use of data set about HCH-contents in soils and food plants in the former GDR and Slovakia

The soil-plant transfer factors and the calculated maximum tolerable soil contents according to the above presented methodology for HCH are given in Table 2:

Soil-plant transfer factors for HCB derived from laboratory studies

Table 2

Food plant	Transfer factor	Maximum tolerable soil content [mg/kg]
oat, corn	0,006	5,7
spring barley, corn	0,004	8,6
spring wheat, corn	0,002	17,2
maize	0,53	4,7
salad	1,36	14,7
radish	2,2	22,7
parsley	1,23	90,3
carrots	0,22	2,7
rapeseed	0,83	0,85
celery	**1,23**	**2,5**
spinach	0,35	10,7

A comparison of the calculated maximum tolerable soil content with the stipulated trigger value for several other pathways as well as with background values shows comparability with background values:

Plausibility check: comparison with trigger and background values

Table 3

Background data (90th percentile)	0,054 mg/kg
Trigger value (path soil – human being, playground)	5 mg/kg
Trigger value (path soil – human being, residential area)	10 mg/kg
Trigger value (path soil – human being, parks)	25 mg/kg
Trigger value (path soil – human being, industrial ground)	400 mg/kg
Calculated maximum tolerable soil content (soil – plant uptake)	**2,5 mg/kg**

Comparison of monitored HCH data in Germany and Moldova, precautionary and trigger values

Germany

Background contents: max. 54 µg/kg dm

Typical concentrations of flood areas: 224 mg/kg dm

Moldova
accumulation in 0…60 cm
α-HCH: 0…22,3 µg/kg dm
β-HCH: 0…75,9 µg/kg dm
γ-HCH: 0…27,5 µg/kg dm
Σ HCH fruit plantagen: 0…20,1 µg/kg dm
grassland: 0…2,4 µg/kg dm
arable land: 0…4,3 µg/kg dm
river sediments: 0…2,4 µg/kg dm
storage of chemicals: 0…125,7 µg/kg dm

Conclusions

The pathway soil-plant is a sensible exposure route due to potential accumulation in the food chain. Precautionary and trigger values for priority organic substances are needed. For non-persistent pollutants their degradation during plant growth should be considered.

It is necessary to initiate common projects independent from specific conditions in different soils and different countries and to harmonise criteria for determination of soil quality.

There is a principle need to derive a precautionary value (0,1 mg/kg) and a trigger value for soil-plant uptake of HCH (2,5 mg/kg).

The calculated values are in the range of monitoring data. The determined trigger value for HCH of 2,5 mg/kg is far below trigger for the path soil – human being.

Furthermore the following activities in the field of soil protection are necessary:

- Harmonization and standardization efforts in soil protection in Central and Eastern Europe.
- Assessment of soil quality, harmonization of strategies for developing of soil values for priority pollutants.
- Generation of data on the current status of soil contamination as a function of the magnitude of contamination, the type of land use and the parent material involved in soil formation.
- Improving knowledge of the contents and dynamics of substances in soils from background territories of different geographical regions.
- Tracing trends in soil contamination by environmental chemicals and monitoring the effectiveness of initiated measurements.
- Equitation of knowledge of the effect and behaviour of substances under different conditions (type of ecosystem, input patterns, pedological, geographical and climatic situation).

References:

1. Aldenberg T, Jaworska JS (2000). Uncertainty of the hazardous concentration and fraction affected for normal species sensitivity distributions. Ecotox Environ Saf 46, 1-18.
2. Anonymus (1998): Federal Soil Protection Act of March 17th 1998 (Federal Law Gazette I, p. 502).
3. Anonymus (1999a): BBodSchV – Federal Soil Protection and Contaminated Sites Ordinance dated July, 12th, 1999 (BGBl. I 1999 S. 1554).
4. Anonymus (1999b): Promulgation of Methods and Standards for Derivation of Trigger Values and Action Values pursuant to the Federal Ordinance on Soil Protection and Contaminated Sites (Bundes-Bodenschutz- und Altlastenverordnung (BBodSchV)), Federal Bulletin No. 161a, August 28th, 1999.
5. Anonymus (1999c): Gefährdungsabschätzung von Umweltschadstoffen. Toxikologische Basisdaten und ihre Bewertung. T. Eikmann, U. Heinrich, B. Heinzow und R. Konietzka (eds.), Loseblattsammlung im Erich Schmidt Verlag.
6. Römbke J, Jänsch S, Schallnaß H-J, Terytze K (2007). Überprüfung der Vorsorgewerte im Hinblick auf den Schutz der Bodenorganismen sowie die Validierung von Bodenuntersuchungsverfahren. Report for the German Federal Environmental Agency (Umweltbundesamt), F+E-Vorhaben Nr. 206 33 206, 63 pp.
7. Terytze, K. und I. Vogel (2007): Kupfer und Zink im Spannungsfeld Nährstoff – Schadstoff bei der landwirtschaftlichen und landbaulichen Nutzung von Klärschlämmen. KTBL-Schrift 453: Perspektiven der Klärschlammverwertung – Ziele und Inhalte einer Novelle der Klärschlammverordnung – BMU-Expertentagung vom 6. und 7. 12.2006 in Bonn, 23-40.
8. Terytze, K.; Kördel, W.; Herrchen, M.; Vogel, I. und A. Nestler (2007): Soil – Plant Transfer of organic chemicals and derivation of trigger values. L. Simeonov and V. Sargsyan (eds.), Soil Chemical Pollution, Risk Assessment, Remediation and Security, 273-283, Springer Verlag.
9. Wilke, B-M., Hund-Rinke, K., Pieper, S., Kratz, W. & Römbke, J. (2003): Entwicklung ökotoxikologischer Orientierungswerte für Böden. Bericht für das Umweltbundesamt, F+E-Vorhaben Nr. 299 71 207. 212 S.

OBSOLETE PESTICIDES AND CONTROL OF ORGANOCHLORINE TOXICANTS IN SOIL

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Succession of actions with obsolete pesticides in the process of inventory of their burial places is considered. Alteration of different quality indexes forms the basis of classification of physically obsolete pesticides according to the rate of their aptitude for application. Investigation of burial places and storages of obsolete pesticides showed the presence of residual quantities of different organochlorine toxicants in soil. In the burial place with forty year-old history, in its upper layer approximately 0.2 mg/kg of p,p'-DDT, 0.18 mg/kg of p,p'- DDE and 0.04 mg/kg of p,p'-DDD were found. The biological test showed how this burial place and former storages of pesticides influence the quality of the drinking water. Study of HCH-isomers persistency in soil revealed that different soils, kind of isomer and duration of its staying in the soil have an essential influence on this index. In past years the probability to discover persistent organochlorine toxicants was typical for soils with burial places and storages of obsolete pesticides and for agricultural lands with perennial plantations.

Key words: obsolete pesticides, burial places, DDT, HCH, soil, control.

The use of pesticides in agriculture and other production spheres creates a number of ecological, toxicological and economic problems. Two main of them are:

1) conservation, migration and accumulation of the pesticide residuals in environment, food and forage;
2) conservation, utilization and elimination of obsolete pesticide stock.

According to different estimations more than 24 thousand tons of spoiled pesticides and agrochemicals exist on the territory of the Russian Federation. Pesticides, which belong to the group of persistent organic pollutants (POPs-pesticides), mostly including DDT, create 10-15% of all identified obsolete pesticides stored on the territory of Russia. At the same time, however, it is marked that about 50% of total obsolete pesticides are unidentified agents and mixtures in which POPs-pesticides can be present. The potential and real ecological and toxicological danger of such pesticides remains rather high.

The solution of the problem of obsolete pesticides supposes to carry out a complex of operations to determine of status and state of these pesticides as well as the following operations with them.

Obsolete pesticides can be divided into 2 categories: 1) physical obsolete, 2) juridical obsolete. Among the first category there are chemicals, permitted for use, but their quality and state have been changed (or could have been changed) during storage after the realization date, violation of storage condition or packing integrity. Among the second category there are chemicals, which use in agriculture or in other production branches is prohibited by law. If obsolete pesticides packing and labels are damaged or absent, determination of the category can be made only after identification of these chemicals.

Possible operations with pesticides, belonging to the first category depend on the result of determination of a complex of indexes, characterizing their composition and properties. Whole criteria, under which the chemicals may be used for consumption are cited in Recommendations [1] and shown in Table 1.

Classification of liquid, powder and suspension pesticides according to the degree of fitness for use at changing their composition or property

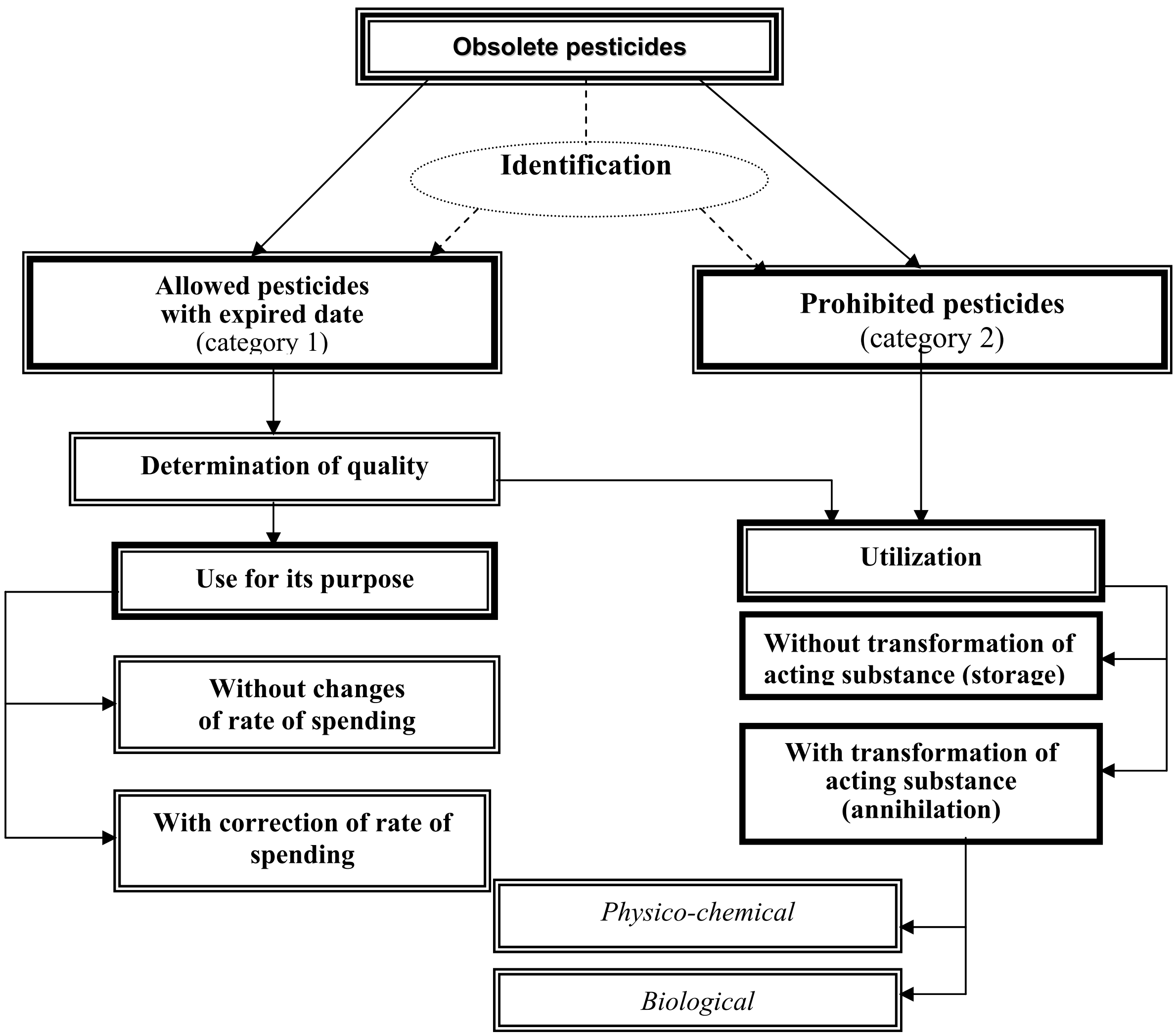
Table 1

Item	Class of fitness		
	I	II	III
	within accepted rate of spending	*with rate recalculation*	*not fit for use*[1)]
Change of pesticide external appearance	without any changes or change is reversible	without any changes or change is reversible	irreversible change
Reduction of mass share of acting substance compared to GOST, TU (respective)	to 10	to 25/30 [2)]	more than 25/30 [2)]

Reduction of water emulsion stability[3)]	increase of oil, cream or sediment volume to no more than 10% respectively	increase of oil, cream or sediment volume to no more than 10% respectively	increase of oil, cream or sediment volume to more than 10% respectively
Reduction of water suspension stability (respective %)[4)]	to 10	to 10	more than 10
Increase of phytotoxicity of working emulsion/suspension	absent	absent	increase compared to standard

Notes:
1) preparation must be discarded in presence of at least one index;
2) the value in numerator is for liquid pesticides, in denominator is for powder or suspension pesticides;
3) index for liquid pesticides;
4) index for powder and suspension pesticides.

The pesticides of the first category or physically obsolete pesticides which belong to class III (Table 1) must be eliminated, and later all operations with them will be analogous to the operations with prohibited pesticides (2nd category of the obsolete pesticides). (See the Scheme).



Scheme of series of actions on determination the status of obsolete pesticides and their treatment

Different methods of disinfection of obsolete pesticides which must be abolished are well known. The most widespread thermal and other physical and chemical methods cause decomposition of their active substances. It is considered that the newly formed products are non-toxic or low toxic and their negative influence on environment may be neutralized completely.

Most of the methods used at present in the Russian Federation are not connected with the transformation of active substances, i.e. the process of obsolete pesticide elimination means their burial. In this connection monitoring of technological condition of the burial place becomes very important as well as a periodic ecological and toxicological control of the area, neighboring to this burial place. Analogous ecological and toxicological control is necessary for those objects where obsolete pesticides are kept (storages, special rooms etc.). In the last case the area, close to such an object, has a high level of pollution even after the pesticides have been eliminated, and it can be the source of the secondary pollution.

Control over the level of accumulation and behavior of the residual quantity of persistent organic pollutants in soil plays an important role in organization and realization of monitoring. As it was mentioned above, in Russia out of all problems with POPs-pesticides, the problem connected with the large-scale use of DDT in past and the existence of its residuals now attracts great attention. Existence of residual quantities in environment, their regional and global migration which were marked during the investigations on the territory of the Russian Federation show how this problem is relevant as regards DDT. A part of other pesticides from the List of POPs-pesticides was used on the territory of Russia restrictedly (Heptachlor, Toxaphene), other pesticides were never included in the List of allowed pesticides in the Soviet Union and later in the Russian Federation (Dieldrin, Endrin etc.). HCH as a potential POPs-pesticide was used actively even not long ago in different forms, so estimation of the influence of its residuals on environment and human health is a task of current importance [2].

According to the control that was conducted by agrochemical experts of the Russian Federation around the places where obsolete pesticides had been buried showed that in most cases residual quantities of some organochlorine toxicants were present. Thus the soils in the West Siberian region of Russia (Tyumenskaya area) close to storages of pesticides as well as agrochemicals were investigated. The residual quantities of organochlorine compounds were found in all of them. In four regions out of fifteen the average content of organochlorine toxicants (total content of DDT-metabolites and HCH-isomers) many times exceeded the rates accepted in Russia (0.1 mg/kg). Three regions out of four were geographically Far North areas [3].

DDT metabolites formation happens both as a process of transformation of *p,p'*-DDT in environment and during keeping DDT chemicals in storages. For example, control over content of active substance and the main DDT metabolites in a chemical with initial content of active substance 10% showed that under the storage conditions the content of *p,p'*-DDT decreased to 6.67% (66.7 g/kg) and metabolite share became 13.04 g/kg for DDE and 20.45 g/kg for DDD within the period of fifteen years. After getting into the environment these metabolites act as independent pollutants.

The conditions of the burial place and the duration of keeping obsolete DDT influence the level of its main metabolites accumulation in soil. It becomes obvious when DDT remains in soil for a long time. The results of the control on the content of residual quantity of DDT metabolites in the burial soil confirm this statement. Typical results were obtained during inspection of a burial place, where obsolete pesticides, mostly DDT had been buried about 40 years before (Table 2). Along with DDT which formed the main part of buried preparation, its metabolites which exceeded the permissible level of their concentration were detected in soil samples. In ground samples, collected from control holes (depth 11 m) insoluble organochlorine toxicants were not detected.

Content of DDT metabilites in soil samples, collected on burial pesticide place

Table 2

Toxicant	Content of metabolite, mg/kg	
	soil [1)]	ground [2)]
p,p'-DDT	0.20±0.04	n/d [3)]
p,p'-DDE	0.18±0.03	n/d
p,p'-DDD	0.04±0.01	n/d

Notes: [1)] 10 samples were chosen from the surface of burial place (the upper layer of soil was 0-25 cm), within a radius of 50 м;

[2)] 2 samples from a control well with depth 11 m situated at a distance of 3 meters from the walls of the burial place;

[3)] n/d – not detected.

A method of biological testing based on pressure of plant pollen under the influence of toxicants was used for integral estimation of the quality of water in connection of the possible negative influence of the investigated pesticide burial place [4]. Data in Table 3 show a clear tendency of changing the general toxicity of water subject to the presence of point pesticide source.

Results of test-control of water samples from different sources taking into consideration the place where pesticides are stored and buried

Table 3

Water source	Place of water source	Result of control (grades)
Hydrant	2 km from pesticide buried	0
Hydrant	3 км from pesticide buried	0
Reservoir of drinking water	imported water (control)	8
Artesian well	1 km from the former pesticide storage (down the slope)	3-4
Well	0.8 km from the former pesticide storage (down the slope)	1-2
Water-pipe water	Rostov-on-Don (control)	7
Water-pipe water	Moscow (control)	7

Note: the scale to estimate the results (grades)
10-8 – good quality of water;
7-5 – water demands additional purification for drinking;
5-3 – the same but with deeper purification;
2-0 – cannot be used for drinking.

Control over the content of HCH-isomers was and remains the obligatory part of monitoring of pesticides in environment. It is carried out by agrichemical departments over the whole territory of the country. While the application of agents containing HCH has been ceased, its traces in soil are found as a rule on the areas where these agents were used in previous years. As with DDT, control over HCH remains relevant during inspections of obsolete pesticide burial places.

Study of HCH-isomers behavior in different soils show that their persistence is different and depend on a great number of factors, including the type of soil. The example of such differences is shown in Table 4 (experiments were carried out in different regions of Russia by agrochemical stations).

Persistence of HCH-isomers in different soils

Table 4

Soil	Content of humus, %	T_{95}, days		
		α-CHC	β-CHC	γ-CHC
Serozem (gray soil)	1.4	435	2020	670
Dark chestnut	3.3	550	4360	690
Black earth	6.6	790	4650	785

A number of experiments show that the speed of isomer HCH detoxication becomes low in the years followed the time when this agent was used. In serozem the meaning of T_{95} (counted exponentially) was 102 days for γ-HCH, and in the following two years the meanings were 630 and 1050 days correspondingly.

At present during any planning or realization of any activity concerning pesticide monitoring in soils and agrosystems top-priority should be given to objects and processes in which presence and participation of strong organochlorine pesticides are highly possible:

1) storage and burial places of obsolete pesticides; 2) soils with perennial plantation where organochlorine pesticides were earlier used; 3) regional and global migration of persistent pesticides by air and by water and their migration with products.

References:

1. Methodic directions for determining the suitability of pesticides for agriculture if their quality has been changed /adopted by Ministry of Agriculture of Russian Federatin 24.07.1995. Moscow.: CINAO, 1995, 23 pp.;

Методические указания по определению пригодности использования в сельском хозяйстве пестицидов при изменении их качества / Утв. МСХ РФ 24.07.1995. М.: ЦИНАО, 1995. 23 с.

2. Lunjov M.I. Pesticides and agrophytocenosis protection. Moscow, Kolos, 1992, 269 pp.; Лунёв М.И. Пестициды и охрана агрофитоценозов. М.: Колос, 1992. 269 с.
3. Kvashnina Ju.A. Pollution of grounds, pesticide storage areas and agrochemicals with ecological toxins. // Agrochemical methods to raise fertility of soils and crops production in adaptive-landscape systems of farming (19-20 April 2006). Materials of 40th International Scientific Conference. Moscow.: GNU VNIIA, 2006, pp.251-253.; Квашнина Ю.А. Загрязнение экотоксикантами земельных участков, территорий складов пестицидов и агрохимикатов // Агрохимические приемы повышения плодородия почв и продуктивности сельскохозяйственных культур в адаптивно-ландшафтных системах земледелия (19-20 апреля 2006 г.). Матер. 40-й Междунар. науч. конф. М.: ГНУ ВНИИА, 2006, с.251-253.
4. Khorkhe R.D., Filina O.N., Klujev N.A., Kourapov P.B. Method of biotesting at the analysis of the spray water quality / Influence of physical and chemical factors on the growth and development of crops. Thesis of the Second High School Conference. Orekhovo-Zuevo, 1996, p. 23.; Хорхе Р.Д., Филина О.Н., Клюев Н.А., Курапов П.Б. Метод биотестирования при анализе качества поливных вод / Влияние физических и химических факторов на рост и развитие сельскохозяйственных культур. Тез. второй межвуз. конф. Орехово-Зуево, 1996, с.23.

ASSESSING THE SEASONAL CHANGES IN THE ORGANOCHLORINE PESTICIDES CONCENTRATION IN THE SEDIMENTS OF ARGES RIVER

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Three sampling campaigns (March, July, October) were performed in order to quantify the concentration trend of organochlorine pesticides such as DDT and its metabolites, HCH (alpha to delta isomers), and few others (endrin, endrin aldehyde, aldrin) in the sediments of the Arges River (lower sector).

Seasonal changes have been determined by the different flow regime (e.g. Flooding in March, reduced amount of precipitation for several months for the October results). Possible explanations are given for the organochlorine compounds presence and evolution over the sampling period.

DDT has been identified as the predominant organochlorine pesticide; the presence of both DDE and DDD in similar concentrations emphasise the appearance of both aerobic and anaerobic metabolisation mechanisms. DDT/DDE and DDT/DDD ratios higher than 1 indicate more recent use of the DDT compared with the time it was officially banned in Romania. Presence of Aldrin, Endrin and Endrin Aldehyde is surprising, as their use has not been reported on a large scale in Romania.

Introduction. Although its use has been officially banned in Romania in 1985 (Cadariu, 2005), DDT and its metabolites (DDTs) remain a constant presence in the environmental samples from Romania, either soils (Covaci et al., 2001), sediments (Covaci et al., 2006; Matache et al., 2006a), food (Hura et al., 1999; Covaci et al., 2004), human serum (Dirtu et al., 2006) or wildlife (Aurigi et al., 2000; Covaci et al., 2006, Matache et al., 2006b). HCH is also mentioned as being one of the main organic contaminants for Romanian rivers (Bujis et al., 1992, Dragan et al., 2006).

The presence/absence of one of the two main metabolites of DDT is determined by the oxygen conditions in the considered environment. Thus, in aerobic conditions, the main degradation product is DDE, while in an anoxic environment DDD is mainly formed (Meikle, 1972; Garrison et al., 2000).

DDT/DDE+DDD ratio is often used for estimating the pesticide time of application, important when aiming to emphasise its illegal use (Tavares et al., 1999, Vashchenko et al., 2005). Depending on its values, the ratio can suggest either old “deposits” of the component (if values < 0.3), or use of the pesticide recent than 5 years (if the ratio exceeds 0.5) (Strandberg et al., 1998). Hung et al. (2004) run a survey on the sediments contamination in the Mekong River delta and concludes that the ratio shows higher values in the vicinity of large human settlements. For HCH isomers, the γ-HCH/α-HCH ratio is used for assessing whether technical HCH (that contains and 55-80% α-HCH and 8-15% γ-HCH) or lindane (>99% γ-HCH) has been used (Corsolini et al., 2006; Li et al., 2006).

The huge anthropogenic pressure that exists here is the reason of choosing this sector of the Arges river watershed – agriculture, hydrotechnical works (before 1989, there were plans of connecting Bucharest with the Danube River through a “transformed” Arges River, adapted for navigation), water supplies (more than 75% of Bucharest water supplies are coming from the Arges River), wastewater receptor (through the mean of Dambovita, one of its main tributaries, the Arges River receives all the wastewater resulted in Bucharest and its metropolitan area).

The present study aimed to determine the occurrence and distribution of several organochlorine pesticides (OCP) in the sediments samples and possible sources of origin, to emphasise seasonal changes in the OCP concentration (spring, summer, autumn), and to perform a semiquantitative risk assessment for the ecosystem by comparison with the *threshold effect level* (TEL) and *probable effect level* (PEL) (TEL and PEL as defined by Smith et al., 1996) for the future evolution of the watershed.

Sampling and methods of analysis. Three sampling campaigns have been performed in order to obtain the samples for this survey, in March, July and October, in order to emphasise possible seasonal changes in the organochlorine pesticides concentration in the Arges River sediments (lower sector). Five sampling points were considered on the Arges River – Gostinari, Hotarele, Radovanu, Clatesti and Danube junction –

chosen so they can provide information on the pesticides sources of origin or emphasise the changes induced in the water chemistry by its main tributaries – Dambovita and Sabar, each of them hosting one sampling point. The sampling points distribution is shown in Fig. 1.

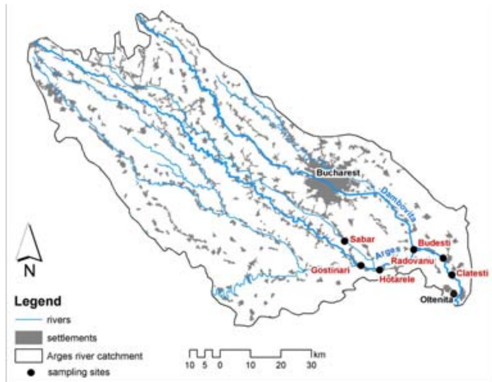

Figure 1. Sampling points location

30 g of wet sediments and 30 g of anhydrous Na_2SO_4 were homogenised in a close vial. After drying, it was well grinded in a pestle and then stirred for 30 minutes in a shaker.

Extraction was performed with light petroleum of chromatographic purity (Merck). The extract was purified on a fluorisyl column (80-100 mesh). The analytes that were consider of interest in the study included: hexachlorocyclohexane – HCH (4 isomers – alpha, beta, gamma, delta), 4, 4’ – dichlordiphenyltrichlorethane (4, 4’ – DDT), 4,4’ – dichlordiphenyltrichlorethylene (4, 4’ – DDE), 4, 4’ – dichlorodiphenyldichloroethane (4, 4’ – DDD), Endrin, Endrin Aldehyde and Aldrin.

Pesticides quantification in the sediments samples has been performed using Electron Capture Detector Gas Chromatography (GC-ECD). A Shimadzu GC 2010 with autosamples **AOC-20 Series** has been used, coupled with an Electron Capture Detector, splitless injector Rtx-CL Pesticides column (Length: 30 m; diameter: 0.25 mm). The injected sample volume was of 1 microliter. The mobile phase was helium. The operational parameters used are: temperature – column 120 ^{0}C, detector – 310 ^{0}C, injector – 250 ^{0}C; pressure **-** . The detection limit of the method was 0.1 ng/g.

Results and discussions.

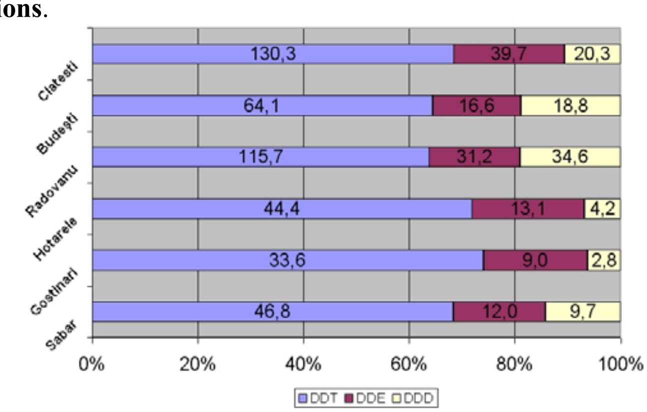

Figure 2. DDTs concentration in the samples collected in March (concentrations in ng/g)

DDT and metabolites. For the sampling campaigns from March and October, DDT is the main contaminant from its group, contributing with more than 60% to the sum of DDTs (Fig. 2 and 4).

For the sampling campaign in July, characterised by reduced flow of the Arges River and its tributaries and a low content of dissolved oxygen (characteristic for the summer months due to increased temperature of water and increased oxygen consumption dueto increased biological activity), it is possible to notice an increased contribution of the DDD isomer (characteristic for low-oxygen environments). In the Radovanu sampling point, where dissolved oxygen concentration did not exceeded 2 mg/L, more than 50% of the

DDTs is represented by DDD metabolite (see Fig. 4).

The same distribution appears for the DDT/(DDE+DDD) ratio. The values registered for March and July are March and October are around 2 or higher (the exception appear in the Budesti and Radovanu sampling points, where dissolved oxygen concentration is low all year long, due to the untreated wastewater released by Bucharest that Dambovita River transports to the Arges River).On the contrary, the ratio values in July are around 1 (minimum = 0.82, maximum = 1.15), which leads to the supposition that the main metabolisation path for DDT in this aquatic system is the anaerobic one.

The high values of the ratio suggests a possible entrance of the DDT in the aquatic system more recent than the period when it was banned in Romania (the half-life time of DDT in moderate climatic conditions is considered to be of about 20 years; Martijn et al., 1993).

HCH isomers. The analysis revealed the presence of all four considered isomers in all the samples considered. No clear trend has been identified for the HCH isomers; though, β-HCH appears to have the highest concentration in most of the samples (10 of 16 samples, with values ranging between 17.63% and 74% of ΣHCH).

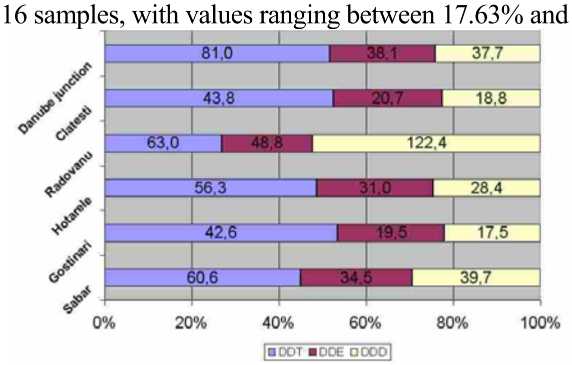

Figure 3. DDTs concentration in the samples collected in July (concentrations in ng/g)

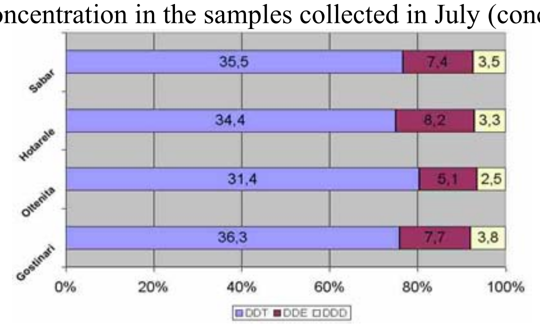

Figure 4. DDTs concentration in the samples collected in October (concentrations in ng/g)

The sum of HCH varied between 6.3 ng/g and 43.9 ng/g, values much higher than those reported by Covaci et al. (2006) for the Danube Delta (from 0.9 to 9.0 ng/g), where β-HCH was present in much lower percentage in the samples, and even missing from some of the samples.

The γ-HCH/α-HCH ratio is higher than 1 in all considered samples, which suggests that lindane was used, pure or as a mixture with other pesticides (e.g. DDT, Baicu and Alexandri, 1973).

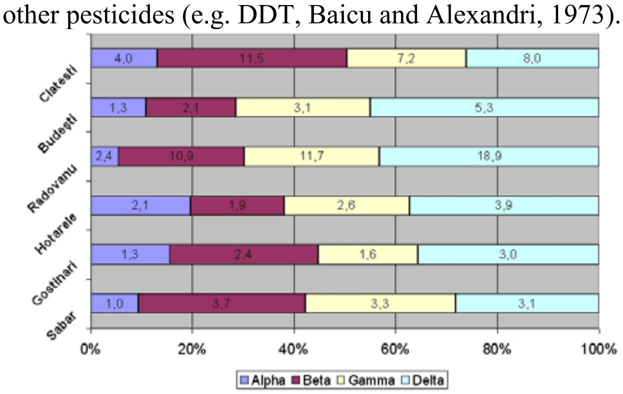

Figure 5. HCH isomers concentration in the samples collected in March (concentrations in ng/g)

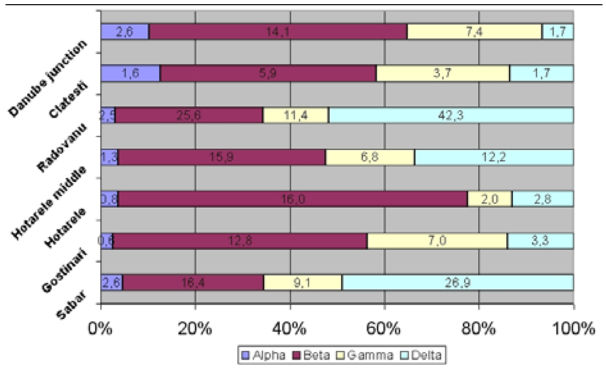

Figure 6. HCH isomers concentration in the samples collected in July (concentrations in ng/g)

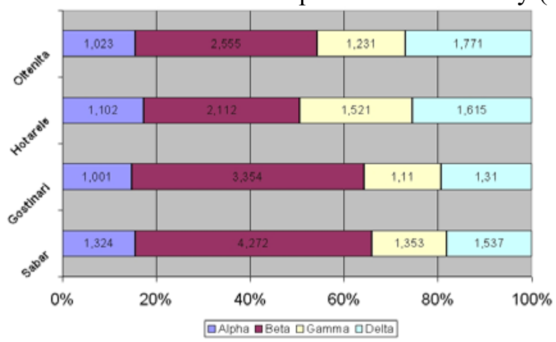

Figure 7. HCH isomers concentration in the samples collected in October (concentrations in ng/g)

Other organochlorine compounds.

The identification of Endrin, Endrin Aldehyde and Aldrin in the analysed samples was really surprising. Their use has not been reported on a large temporal scale in Romania and only for short periods of time (1975-1980) (Cadariu 2005).

The concentration range is quite wide for all three compounds: Aldrin – 0.99 and 40.98 ng/g, Endrin – 1.21 and 102.87 ng/g, Endrin Aldehyde – 2.19 and 29.44 ng/g. The high concentration of Endrin (registered in March) might be connected with the flooding that affected the Arges River watershed during the sampling period. Extreme phenomena tend to determine the remobilisation of sediments that were embedded in the riverbed many years prior to their reintroduction in the aquatic system. A similar process is generated by the surface runoff, which transports soil particles (possible to be contaminated) into the river that are either joining the upper level of the sediments deposits or transported on long distance as suspended matter.

Comparison with the TEL and PEL. As references we used the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (CCME, 2002), which are displayed in Table 1.

The values meeting the guidelines are as it follows: DDT – all 16 samples exceed the PEL, DDE – 1 sample out of 16 meets the PEL, DDD – 4 samples concentrations are below the TEL, 6 samples meet the PEL requirements, gamma-HCH – 3 samples out of 16 meet the

PEL requirement, Endrin – 5 samples are below the TEL level, 1 sample exceeds the PEL.

TEL and PEL for the considered compounds

Table 1

Compound	TEL	PEL	Compound	TEL	PEL
DDT	1.19	4.77	Gamma- HCH	0.94	1.38
DDD	3.54	8.51	Aldrin	NG	NG
DDE	1.42	6.75	Endrin	2.67	62.4
Alpha-HCH	NG	NG	Endrin Aldehyde	NG	NG
Beta-HCH	NG	NG			

* *NG – No Guidelines available*

Conclusions.

The Arges River lower sector is a highly contaminated ecosystem, the analysis of sediments samples revealing long-term pollution due to the economic activities (mainly agricultural ones).

Despite the official ban enforced more than 20 years ago, DDT is still the most important contaminant of the Arges River aquatic sediments. Its metabolisation is rather reduced (the ratio with its metabolites is higher than 1) so it is likely it entered the aquatic system more recently. Gamma-HCH is also present at levels that could generate an ecological risk for the aquatic life.

The presence of the organochlorine contaminants at concentrations exceeding in some cases the PEL poses a great risk for the living organisms. Furthermore, dredging the river for transforming it in a navigation channel might generate ecological issues due to the remobilisation of pollutants from the riverbed sediments into the river water and subsequently increase their bioavailability.

Acknowledgements.

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References:

1. Aurigi, S, Focardi, S, Hulea, D, Renzoni, A (2000), Organochlorine contamination in bird's eggs from the Danube Delta, Environmental Pollution 109, p. 61-67.
2. Baicu, T., Alexandri, Al., V., Îndrumător pentru folosirea pesticidelor, Ed. Ceres, Bucureşti, 1973, 148
3. Bujis, L, Uzunov, Y, Tcankov, K, Water quality profile of the Danube river along the Bulgarian-Rumanian stretch (1992), ICWS Report, Amsterdam, The Netherlands.
4. Cadariu, A (2005), Romania – Country Situation Report on POPs, http://eea.ngo.ro/materiale/CSR_final_eng.pdf
5. Canadian Council of Ministers of the Environment (2002), Canadian Sediment Quality Guidelines for the Protection of Aquatic Life, www.ccme.ca/assets/pdf/e1_06.pdf.
6. Corsolini, S, Covaci, A, Ademollo, N, Focardi, S, Schepens, P (2006), Occurrence of organochlorine pesticides (OCPs) and their enantiomeric signatures, and concentrations of polybrominated diphenyl ethers (PBDEs) in the Adélie penguin food web, Antarctica, Environmental Pollution 140 (2), p. 371-382.
7. Covaci, A, Gheorghe, A, Hulea, O, Schepens, P (2006), Levels and distribution of organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in sediments and biota from the Danube Delta, Romania, Environmental Pollution 140, 136-149.
8. Covaci, A, Gheorghe, A, Schepens, P (2004), Distribution of organochlorine pesticides, polychlorinated biphenyls and a -HCH enantiomers in pork tissues, Chemosphere, Vol. 56 (8), p. 757-766.
9. Covaci, A., Hura, C, Schepens, P (2001), Selected persistent organochlorine pollutants in Romania, The Science of the Total Environment, Vol. 280 (1-3), p. 143-152.
10. Dirtu, AC, Cernat, R, Dragan, D, Mocanu, R, Van Grieken, R, Neels, H, Covaci, A (2006), Organohalogenated pollutants in human serum from Iassy, Romania and their relation with age and gender, Environment International, Vol. 32 (6), p. 797-803.
11. Dragan, D, Cucu-Man, S, Dirtu, AC, Mocanu, R, Van Vaeck, L, Covaci, A (2006), Occurrence of organochlorine pesticides and polychlorinated biphenyls in soils and sediments from Eastern Romania, International Journal of Environmental Analytical Chemistry Vol. 86 (11), p. 833-842.
12. Garrison, AW, Nzengung, VA, Avants, JK, Ellington, JJ, Jones, WJ, Rennels, D and Wolfe, NL, Environ. Sci. Technol. 2000, 34: 1663 – 1670.
13. Hung, MN, Kajiwara, N, Kunisue, T, Subramanian, A, Iwata, H, Tanabe, S, Hung, VP, Cach, TB (2004), Contamination of persistent organochlorines in sediments from Mekong River Delta, South Vietnam, Organohalogen Compounds, Vol. 66, p. 3664-3669.
14. Hura, C, Leanca, M, Rusu L, Hura BA (1999), Risk assessment of pollution with pesticides in food in the Eastern Romania area (1996-1997), Toxicology Letters, Vol. 107 (1), pp. 103-107
15. Li, J, Zhang, G, Qi, S, Li, X, Peng, X (2006), Concentrations, enantiomeric compositions, and sources of HCH, DDT and chlordane in soils from the Pearl River Delta, South China, Science of the Total Environment 372, p. 215–224.
16. Martijn, A. Bakker, H. and Schreuder, R. H.: 1993, Bull. Environ. Contam. Toxicol. 51, 178.
17. Matache, ML, Ioja, C, Hura, C, Rozylowicz, L (2006a), Organochlorine Compounds (DDT, HCH) Concentration In Sediments Collected From The Lower Sector Of The Arges River, Romania, Organohalogen Compounds Vol. 68, p. 436 – 439.
18. Matache, ML, Rozylowicz, L, Hura, C, Matache, M (2006b), Organochlorine Pesticides – a Threat on the Herman's Tortoise Perpetuation, Organohalogen Compounds Vol. 68, p. 728 – 731.

19. Meikle, RW, 1972, Decomposition: Qualitative Relationships in Organic Chemicals in the Soil Environment, Vol. 1, Goring, C. A. I. and Hamaker, J. W. (eds.) Marcel Dekker, New York.
20. Smith, SL, MacDonald, DD, Keenleyside, KA, Ingersoll, CG, Field, J, J. Great Lakes Res., 1996, 22: 624–638.
21. Strandberg, B, van Bavel, B, Bergqvist, P-A, Broman, D, Ishaq, R, Näf, C, Pettersen, H, Rappe, C (1998), Occurrence, Sedimentation, and Spatial Variations of Organochlorine Contaminants in Settling Particulate Matter and Sediments in the Northern Part of the Baltic Sea, Environ. Sci. Technol., Vol. 32 (12), p 1754 – 1759.
22. Tavares, TM, Beretta, M, Costa, MC (1999), Ratio of DDT/DDE in the All Saints Bay, Brazil and its use in environmental management, Chemosphere, Vol. 38 (6), p. 1445-1452.
23. Vashchenko, MA, Syasina, IG, Zhadan, PM (2005), DDT and Hexachlorocyclohexane in Bottom Sediments and the Liver of Barfin Plaice Pleuronectes pinnifasciatus from Amur Bay (Peter the Great Bay, the Sea of Japan), Russian Journal of Ecology, 36 (1): 57–61.

BIOMBIENCE AS AN INDICATOR OF CONTAMINATION THE ENVIRONMENT BY CHLOR-ORGANIC PESTICIDES IN CONDITIONS OF SOUTH OF THE KYRGYZ REPUBLIC

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Contamination of the environment by pesticides, and in the first instance, by chlor-organic ones, i.e. persistent organic pollutants (POPs), in conditions of south of the Kyrgyz Republic has become one of the basic causes, leading to the rise of genepathologies – malignant tumours, particularly, reproductive system in women, innate vices of development and uterine pathologies, man and women sterility and impotence. It also causes the rise of sick rate and, in the first instance, in women and children, deterioration of the course of pregnancy and delivery, causing the birth of weak, defective children. As a whole, it leads to the shortening of the lifetime and deterioration of the genefond of the population [6,7].

Frequently, it is very difficult to determine the areas contaminated by pesticides on account of vast spaces. Such investigations require carrying out numerous, labour – consuming and expensive analyses. Kyrgyzstan has no funds for carrying out continuous monitoring these technogenic processes. Therefore, we have to search for more available, economically advan- tageous, and at the same time, informative ways on exposure the hotspots in pasture and mountain zones.

Establishment of such problematic areas connected with environment condition, could give a perspective to reduction of sickrate and improvement of genefond.

With that end in view we have developed the measures on neutralization and removing pesticides from organism. For this purpose we apply medicines exctracted from local herbs and fruits (rich in vitamins and biologically active elements), water from mineral springs. We also study the possibilitres of the production ecologically pure meat and dairy products for population. Producers of the Kyrgyz Republic (cattle-breeding country) could export ecollogically pure products, getting profit.

Materials and methods of study. One of the characteristics of chloric-organic pesticides (COPs) is a marked capacity to be accumulated in the tissues and fats of animals when getting into the organism in small amounts and be removed from the organism with urine, faeces, bile [3,4] and milk, aswell. The studies of some authors [5] showed, that even though COPs are found in the environment in scant amounts, the COP concentration in the tissues of animals increases in several times.

Therefore, the most optimum way of the determination the level of contamination the environment by pesticides is determination of COP concentration in bioambience (e.g. milk, adipose tissues of animals – cows, goats, sheep, yaks, mares). When selecting the animals for study the following factors were took into consideration: natural and agrotechnical characteristics of the fields, where the cattle grazed, sources of forage (local or import), chemical pest- and weed-killers, sea level. Plain pastures, mountain rocks and glaciers have been embraced in our study.

For investigation we selected animals that had no contact with pesticides and grased on various pastures, located on different heights above sea level. The maps of investigation were designed.

Milk of the cows, grasing on the plains, in mountain and low land areas was studied.

The area of cow pasture is about 6-9 km^2, mear pasture – 20-25 km^2, sheep pasture -12-15 km^2.

Goats live on the rocky slopes, on different heights above sea level. Yaks are the most Alpine animals in our conditions (from 2,5 th.m. above sea level in winter , and 4,5-6,5 th.m.– in summer). Frequently, the yaks drink melted snow.

When conducting the analyses we took into account that animals and their cattle – sheds were not treated with pesticides, and that animals were fed with extra forage from other places. The materials for investigation were the first and the last portions of milk (20-50 ml.) and inner adipose tissue of the cattle (50gr.).

The analysis on the COP content (DDT,DDE,DDD,GHCG, aldrin, dildrin) was conducted by means of method of thin – layer gas – liquid chromatography, developed by collaborators of USRIHT (Kiev) Girenko D.B., Klisenko M.A., 1971.

When investigating milk and adipose tissue of animals depending on the area (groups of animals) we took into consideration that COPs could be blow away at the distance of 20-30 km. and could be preserved up to 50 years [2,5].

Materials for study were divided into 5 groups:

I group: milk of cow, inner adipose tissues, taken from cows, goats, sheep, mears, grazing near arable lands.

II group: milk, inner adipose tissues, taken from cows, goats, sheep, mears, grazing in lowlands, near arable lands, located behind high hills, i.e. so – called inaccessible areas for pesticides.

III group: cows, mears, goats, sheep, yaks, grazing on the areas, where in 1982-1983 pesticide DDT was applied.

IV group: cows, mears, goats, sheep, yaks, grazing on the areas near the plains, where the pesticides were intensively applied or are applying for the present time.

V group: cow, mears, goats, sheep, yaks, grazing on the areas isolated from the plains, i.e. behind the mountain ridge, in comparatively inaccessible areas.

The more detailed data are presented in Table 1.

List of analyses of milk and adipose tissue of animals

Table 1

№	**Animals**	**Total analyses of milk and inner fat of animals according to the groups**										**Total analyses**	
		I		**II**		**III**		**IV**		**V**			
		M	IF	M	IF	M	IF	M	IF	M	IF	M	IF
1	Cows	2	2	2	2	2	2	2	2	2	2	10	10
2	Sheep	-	2	-	2	2	2	2	2	2	2	6	10
3	Mears	-	2	-	2	2	2	2	2	2	2	6	10
4	Goats	-	2	-	3	3	3	3	3	3	3	9	15
5	Yaks	-	-	-	-	3	3	3	3	3	3	9	9
	Total	2	8	2	9	12	12	12	12	12	12	40	54

M-milk IF-inner fat

The data received and discussion

Taking into account that in the 2 nd and 5th groups were the animals grazing on ecologically pure zones, the data received are presented in Table 2.

List of COPs revealed from milk and adipose tissue of animals (2,5 groups)

Table 2

№	Animals	II-group						V-group					
		Milk			Inner fat			Milk			Inner fat		
		Total tested	Total revealed	%	Total tested	Total revealed	%	Total tested	Total revealed	%	Total tested	Total revealed	%
1	Cows	2	1	50,0	2	1	50,0	2	-	-	2	-	-
2	Sheep	-	-	-	2	1	50,0	2	-	-	2	-	-
3	Mears	-	-	-	2	-	-0	2	-	-	2	-	-
4	Goats	-	-	-	3	1	33,3	3	-	-	3	-	-
5	Yaks	-	-	-	-	-	-	3	-	-	3	-	-
	Total	2	1	50,0	9	3	33,3	12	-	-	12	-	-

In the second group the elements of GHCG were found in cow milk, as well as in inner fat – GHCG and DDE, in sheep's fat – GHCG.

The presence of two types of pesticides in cow milk, is probably connected with the fact, that the cow regularly grazed in lowlands, while the goats and sheep– on mountain pastures (in summer), i.e. in ecologically pure zones.

Table 3 comprises 2 groups, the 1st and the 4th,i.e. the animals, grasing on the territories treated with pesticides, but it should be taken into account that the 1st group was located in lowlands, at distance of 15-25 km. from arable lands.

In the 4th group animals grased in the mountains (160-190 km.distance from the plain). This area is located in the upper reaches of the river.

List of COPs revealed in milk and adipose tissue of animals (1,4 groups)

Table 3

№	Animals	I- group						IV- group					
		Milk			Inner fat			Milk			Inner fat		
		Total tested	Total revealed	%	Total tested	Total revealed	%	Total tested	Total revealed	%	Total tested	Total revealed	%
1	Cows	2	1	50,0	2	1	50,0	2	-		2	1	50,0
2	Sheep	-			2	1	50,0	2	-		2	1	50,0
3	Mears	-	-	-	2	-	-	2	-		2	-	-
4	Goats	-	-	-	2	1	50,0	3	-		3	-	-
5	Yaks	-	-	-	-	-		3	-		3	-	-
	Total	2	1	50,0	8	3	41,6	12	-		12	2	16,6

I group: GHCG was found in milk of one cow (0,004 mg/kg).In inner fat of
cow-GYCG-0,008 mg/kg
sheep-DDE-0,009 mg/kg
goat**-** DDE-0,004 mg/kg

Pesticides could probably get into the soil by wind rose.

Table 4 presents the data of the 3d group of animals grazing on pastures, where in 1982-1983 pesticides were applied.

List of COPs in milk and adipose tissue of animals (3 group)

Table 4

№	Animals	III-group					
		Milk			Inner fat		
		Total tested	Total revealed	%	Total tested	Total revealed	%
1	Cows	2	1	50,0	2	1	50,0
2	Sheep	2	1	50,0	2	1	50,0
3	Mears	2	1	50,0	2	-	
4	Goats	3	-	-	3	-	
5	Yaks	3	-	-	3	-	
	Total	12	3	25,0	12	2	16,66
	Soil from marmot hole	3	1	33,3			

DDE was found in milk of cows, sheep, mears and in adipose tissue of cows (0,004 mg/kg), sheep (0,002 mg/kg). DDT was found in the soil taken from marmot holes (0,001mg/kg). DDE - in milk of cow, mears and goats, that confirms Z.N.Bogomolova and A.I.Shtenberg assumption concerning conversion of more toxic DDT into less toxic DDE.

III grop: DDE was found in milk of mear, but there were no traces in adipose tissue. It is quite possible, that animals had temporary nervous stress and throw of pesticides in blood. Pesticides can be possibly removed from organism with milk, urine, bile, faeces, but this problem needs special purposeful stady.

Thus, bioambiensces: milk, adipose tissue of animals is quite relable indicators of the contamination the enviroment by COP. The method can be applied for determination pesticide defective areas.

References:

1. Bogomolova Z.N., Shtenberg A.I. "Content of chlor organic pesticides in some organs, tissues, milk", Hygenic and biological aspects of pesticides use in conditions of the CENTRAL ASIA and Kazakhstan, Materials of the All-Union Symposium, Dushanbe, September 1978, edited by ac. AMN SSR prof. Medved L.N., ac. AMN SSR prof.

Narzukulov M.N. Edition. "Donish" Dushanbe 1978, S. 65-67.
2. Belonozhko G.A., Kuchak YU.A., Sorokina L.V., Tovstenko A.I., Vivchurko S.N., Subbotina S.B., Petrichenko L.N. About approaches to hygenic estimation of the methods and ways of pesticide use in connection with danger of their spreading into external amsience, Problems of pesticide hygiene and toxicology, M1970 S.244-247).
3. Kagan YU.S. "General toxicology of pesticides" Kiev, 1981. P. 176.
4. Lyubomudrov V.E., Kitaev M.N. "Pesticide intoxication" Edition "Kyrgyzstan" 1972.
5. Spynu E.I., Antonovich E.A., Vrochinskiy K.K., Molozhanova L.G., Stefanskiy K.S., Hygenic importance of the accumulation and circulation of POPs, Problems of pesticide hygiene and toxicology, M1970 C.212-218).
6. Toychuev R.M. Institute of Medical Problems. -Bishkek: "Ilim", 2004. -80 p.
7. Toychuev R.M. Medical and ecological problems of the south of Kyrgyzstan, Central-Asian Medical Journal, April, 19-21 Osh-2007, P.22-25

MALIGNANT TUMOURS OF WOMAN'S REPRODUCTIVE SYSTEM AS AN INDICATOR OF CONTAMINATION THE ENVIRONMENT BY CHLOR-ORGANIC PESTICIDES (COPS) IN CONDITIONS OF OSH REGION

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Contamination the environment by chemical pest- and weed-killers is one of the global ecological problems. Chemical pest- and weed-killers have become one of the main causes of sick rate increase. In view of aforesaid, Stockholm Convention was adopted. The Convention takes notice of this fact and demands the states ratified the Convention to be involved in the control for chemicals use.

Meantime, tranference the lands to private sector, use of former landing grounds and chemicals storehouses create extra difficulties for such control. At present chemical pest- and weed-killers are used in various agro- technologies by private traders, who are not aware of their use, sanitary and safety standards. In this connection a number of contaminated zones have rapidly increased. On the other hand, the population has started cultivating various vegetables and melons on the territories of former tobacco- and cotton plantations, i.e. on the territories contaminated by pesticides.

According to our data, contamination the environment by chlor- organic pesticides (GHCG, DDT, DDE, DDD, alderin, dilderin) has become one of the causes of increase the number of breast cancer cases among the women with many deliveries in Osh region [2,3].

The factors mentioned above have become not only ecological problem, but social, economic, medical as well. Monitoring the arable lands is one of the ways out. But at the same time carrying out monitoring the contamination of soil and food products on vast territories is still problematic.

Farmers have no funds for carryung out numerous and expensive analyses.It is necessary to develop new convincing ways of determination the most dangerous areas contaminated by pesticides and their influence the sick rate of the population, including malignant tumours of woman's reproductive system. It would convince the private traders to carry out monitoring their arable lands for getting ecologically pure products, and, in prospect, not only for their own need, but for export as well.

Materials and methods of study. For determination the hotbeds of pesticide concentration and the degree of contamination danger we have applied epidemiological and toxicological methods. Medical data (Osh region) for the last 15 years (1992-2006) have been analyzed for studying the tumours of woman's reproductive system. Determination of COPs (GHCG, DDT, DDE, DDD, aldrin, dildrin) content in tumour tissues has been carried out using the methods of thin-layer gas-liquid chromatography (developed by D.V. Girenko and M.A. Klisenko, 1971)

The data received and discussion. The dynamics of sick rate of women with breast cancer (BC), cervix uteri cancer (CUC), body uteri cancer (BUC), ovary cancer (OC) are shown in Table 1

The dynamics of sick rate of women with cancer of reproductive system (100 th. women)

Table 1

Years	BC	CUC	BUC	OC	Total
1992	5,231	4,65	2,52	1,74	14,14
1993	5,69	5,12	1,14	1,89	13,84
1994	7,491	3,55	1,5	1,48	14,02
1995	5,70	5,15	1,47	2,20	17,05
1996	5,928	7,18	1,97	2,15	17,23
1997	5,65	4,24	2,3	1,59	13,78
1998	6,92	3,46	1,38	2,94	14,7
For 7 years	6,087	4,76	1,75	1,99	14,59

1999	10,51	5,93	1,52	2,37	20,33
2000	6,49	5,16	1,33	1,83	15,25
2001	7,0578	6,07	1,14	2,29	16,56
2002	7,27	6,95	2,10	1,61	17,93
2003	7,973	7,02	1,11	1,75	17,86
2004	7,3	6,27	1,72	1,41	16,7
2005	9,28	9,74	1,54	3,24	23,8
For 7 years	7,982	6,73	1,49	2,07	18,28
Increase	+1,895	+1,97	-0,26	+0,08	
2006	7,19	11,17	1,99	3,28	24,17

As it is seen from Table 1, the rapid increase in all groups has been observed in 1999. This fact has close connection with the year 1998, when the lands were transferred to private sector. Vegetables, melons and leguminous plants were cultivated on the fields contaminated by chlor- organic pesticides. In this connection COPs penetrated in the organism of women through the food products. COPs accumulated in adipose tissues of breast, cervix uteri and ovary and caused the formation of free radicals with a great energy.

Superfluous energy leads to accelerated cell-division, i.e.to formation of the tumours.Excessive accumulation of pesticudes in organism of pregnant women and foetus leads to cell destruction, i.e. to formation of innate vices of development in children.

Muscular tissue accumulates COPs in less amounts, therefore the number of BUC cases has decreased, whereas in Uzgen region it has rapidly increased. Women of this region are engaged in rice-growing. The concentration of COPs in rice waters is very high. COPs penetrate in the organism of rice-planters (women) through integument.

Sick rate of women with breast cancer depending on the regions and the degree of contamination the environment by COPs

Table 2

№	Regions	Zones	Sick rate of women with breast cancer		
			1992-1997	1998-2003	2004-2006
1	Karasuu	Cotton-growing	6,43	8,635	8,64
		Mountain	0,545	0	0,99
		Total	5,2	7,02	7,05
2	Aravan	Cotton-growing	3,9	6,12	10,26
		Mountain	-	-	-
		Total	3,28	5,46	8,66
3	Nookat	Tobacco- growing	3,88	5,60	8,27
		Mountain	1,02	-	-
		Total	3,4	4,77	6,89
4	Uzgen	Tobacco- growing	2,52	7,7	7,28
		Mountain	1,88	2,7	-
		Total	2,4	6,5	5,96
5	Karakulzha	Tobacco- growing	2,41	7,66	11,73
		Mountain	0,866	1,65	1,6
		Total	1,66	5,00	6,65
6	Alay	Gulcho (pesticides store house)	-	6,84	20,92
		Zhany – Alay	-	12,76	-
		Pure zone	0,68	0,60	3,8
		Total	0,51	2,54	7,46

As it is shown from Table 2, the sick rate in cotton-growing zones is higher as compared with tobacco-growing and ecologically pure mountain zones. The number of cases in Alay region has increased since 1992

(0,51 up to 20,92 cases, 100 th. women). In course of study the reasons of the number cases increase we have found out that the inhabitants of Janyalay region were engaged in cattle-breeding. In 1998 stock-raising farms broke up and the lands where fodder crops had been cultivated were tranferred to private sector. The inhabitants started cultivating cotton and tobacco, using pesticides. Therefore, the number of cases in Alay regin has increased.

In 1997-1999 in Gulcho over 3 hectars of the lands with former chemical storehouse were allotted among private traders for housebuilding and gaderns. About 70 families settled there.

Moreover, sewage from their gaderns ran to the houses located below and were used for watering the gaderns, everyday necessities and for animals, including milch cows.

When testing the soil and water from the territory of former storehouse, GHCG was found in the soil (0,13-1,28 mg/kg) and DDE - in the water (0,0007 mg/kg).

The studies of tumour tissues, removed by operation (last 6 years) showed concentration of COPs (over 0,1 mg/kg) in 45 women (many deliveries), in 30 women-83,7% (several deliveries). COPs were found in tumour tissue of uteri as well (15 women-66,66%).

Thus, sick rate of women with reproductive system cancer correlates with contramination the environment by COPs. In conditions of local increase of sick rate of woman's reproductive system cancer it is necessary to arrange search of areas contaminated by pesticides and to undertake appropriate measures on maintenance the health of population using local medicines, and, in the first instance, antioxidants.

References:

1. D.B. Girenko and M.A. Klisenko. Methods of determination the micro amounts of pesticides in food products, forages, and external ambience. (Methodological recommendations) prepared by colloborators of VNIIGINTOKSA. Kiev. 1971. Moscow. - 1971. Part. 5. P 11-25.
2. National plan on the execution of Stockholm Convention on POPs. - Bishkek, 2006. -50 p.
3. R.M. Toichuev. Institute of Medical Problems. - Bishkek: Ilim, 2004. -80 p.

ASSESSMENT OF DAIRY PRODUCTS' LEVEL OF CONTAMINATION WITH ORGANOCHLORINE PESTICIDES

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Introduction

In the sixties – eighties of the past century, organochlorine substances (aromatic chlorinederived hydrocarbons (DDT), polychlorindiene (aldrin, dildrin, heptachlor), polychlorterpene (toxafen, policlorpinen), acyclic chlorinederived hydrocarbons (HCH)) were widely used in agriculture as insect-acaricides and fungicides. The usage of pesticides in pest control generates a range of risks for human and animal health. Due to liposolubility and persistence of these substances they are accumulated in the adipose tissue and penetrate the milk (including breast milk), being dissolved in its fat phase.

The problem of global POPs (persistent organic pollutants) – related pollution and morbidity increase is raised because of two serious characteristics of the given substances: 1) they can be spread on large distances from the place of their application and ii) they are accumulated while moving along the food chains.

One of the priority directions in the investigation of the pesticides-related risk for the environment and human health is the assessment of the level of pesticides entrance in human organism. For the major part of the population the main source of exposure to organochlorine pesticides is the dietary intake. Among the various dietary components, consumption of contaminated cow's milk and sour dairy products can be the foremost path of exposure to POPs. Among different age groups of the population, children, especially of early and young age, for whom milk and dairy products are the basic and indispensable part of the intake, are the most susceptible to the influence of organochlorine pesticides (OCPs).

A complex monitoring of obsolete pesticides was not carried out in the Republic of Moldova for the last ten years. To our knowledge, the information about the current OCPs contamination status of cow's milk is very scarce, while data on the level of organochlorine pollutants in sour cream and curd is absent.

The aims of the investigation reported in this paper were:

- to evaluate the current extent of OCP contamination in the whole cow's milk, sour cream and curd from different localities in south, center and north of Moldova;
- to determine factors those influence the levels of contamination.

Materials and Methods.

Chemical analysis was performed in the National Scientific and Practice Centre of Preventive Medicine, which regularly participates in external quality control studies.

The samples of cow's milk, sour cream and curd were collected in 2005 and 2006 (n=91) from the cattle owners from 8 localities of southern, central and northern zones of the republic. Samples of cow's milk, sour cream, curds and cheese were investigated. The extraction methods used for determinations of the residues of DDT and metabolites, HCH and isomers, heptachlor, dicofol and hexachlorobenzene (HCB) were identical. Qualitative and quantitative determinations in purified sample extracts were performed by capillary gas chromatography with an electron capture detector. The number of total analyzes effectuated is 819.

Results and Discussions

It was determined that 49.5% of the analyzed samples, including 25.6% of milk, 86% of sour cream and 25% of curds and cheese samples contained OCPs residues.

Cow's milk (39) - more than 25% samples contained OCPs residues; 25.6% of which included DDE, 2.56% - β- and γ- HCH. Dicofol, heptachlor and HCB were not detected in milk samples.

Sour cream (36) - more than 86% samples contained residues of DDT, in the form of metabolites: 68.3% - DDE, 2.78% - DDT and DDD. The isomers of HCH were established in 22.2% of samples: 22.2% held β-HCH, 8.3% - α-HCH and 11.1% - γ- HCH and heptachlor. Dicofol and HCB were determined in 5.55%.

Curds (16) – the residues of DDT (in form of metabolites DDE) were detected only in the cheese sample. 12.5% of samples contained dicofol and 6.25% - γ- HCH.

The results of our research (presented in the Table 1) show that the highest concentrations of DDT (sum of metabolites) and HCH (sum of isomers) were found in the sour cream samples and the lowest level - in the milk.

The OCPs can be listed in accordance with the frequency of determination: the first place is occupied by a metabolite of DDT – DDE < HCH < heptachlor< dicofol < hexachlorbenzene.

The content of the OCPs residues in the milk and dairy products

Table 1

Pesticide	Milk (mg/kg brut)	Sour cream (mg/kg brut)	Curds (mg/kg brut)
DDT	0	0,001-0,0095 (1/36)	0
DDE	0,0002- 0,005 (10/39)	0,002- 0,04 (21/36)	0,008 (1/16)
DDD	0	0,005 (1/36)	0
α-HCH	0	0,0006- 0,0015 (3/36)	0
β-HCH	0,001 (1/39)	0,002 - 0,02 (8/36)	0
γ-HCH	0,0002 (1/39)	0,001- 0,004 (4/36)	0,002 (1/16)
Heptachlor	0	0,001 - 0,008 (4/36)	0,006 - 0,017 (2/16)
Dicofol	0	0,009 - 0,079 (2/36)	0
HCB	0	0,002 - 0,003 (2/36)	0

The most polluted dairy product is sour cream. The established concentrations of the mentioned pesticides in creams were 10-100 times higher in comparison to milk (figure 1).

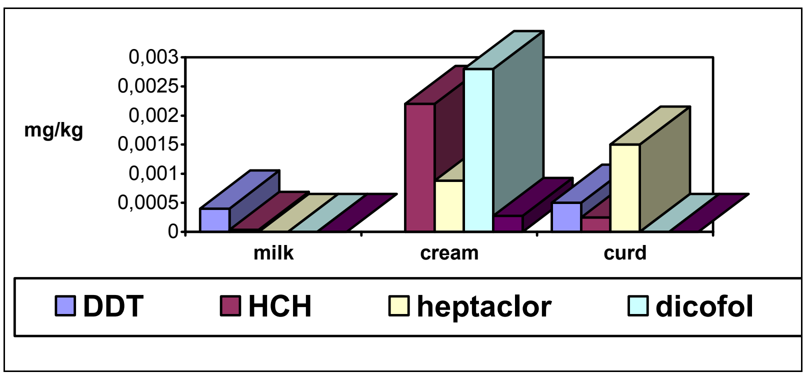

Figure 1. The content of OCPs residues in dairy products.

The comparison of the assessed levels of dairy products' contamination with OCP in different regions of the republic showed that concentration of DDT is higher in samples collected in the South and Center of the Republic of Moldova, while the residual level of HCH, dicofol, and HCB were sensed mostly in the samples from northern parts of the republic (Figure 2, 3). We presume that this fact is linked to the specifics of agricultural production.

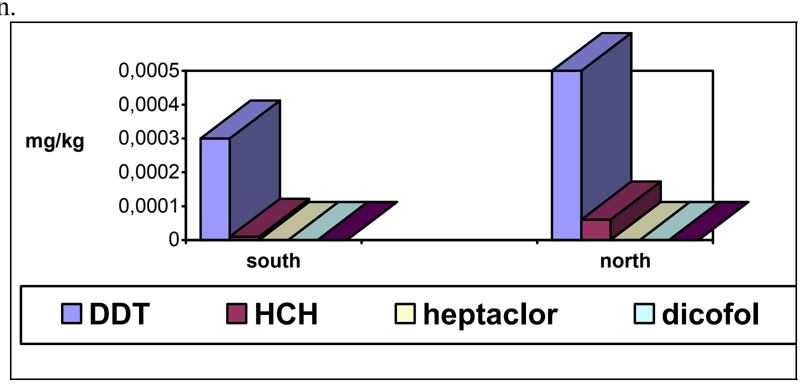

Figure 2. The content of OCPs residues in milk according to the zones of the republic.

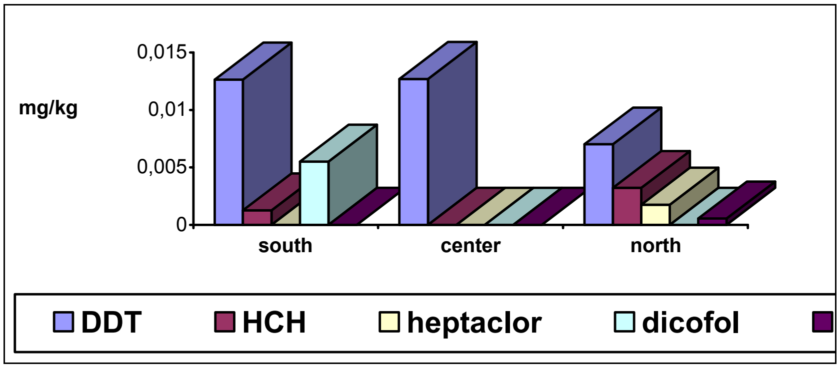

Figure 3. The content of the OCPs residues in sour creams according to the zones of the republic.

The detected concentrations of the pesticides did not exceed the MRL, except for heptachlor (its residues are not admitted in food).

We have calculated the possible level of OCPs intake, taking into consideration the daily dietary intake of milk and dairy products, which is equal to 1225 mg/day (calculated on milk). The potential summary daily intake of the HCH is 0.003 mg/kg, and DDT – 0.0127 mg/kg. The same can be said about the presumable level of dicofol and HCB receipt (0.003 mg/kg body weight/day). The average quantity of heptachlor that can enter the human organism together with milk and dairy products is equal with 0.0011 mg/kg b.w./day.

Conclusions

Thus, despite the determination of the OCPs in concentrations significantly lower than the admissible levels, and taking into consideration the persistence of these compounds and their tardive effects, besides the monitoring of their presence in the environmental objects and food, the assessment of the population's health is required in order to prevent OCPs possible negative influence.

CONTENTS OF ORGANOCHLORINATED PESTICIDES AND POLYCHLORINATED BIPHENYLS IN SOIL AND SEDIMENTS IN REPUBLIC OF MOLDOVA

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Contamination of soil is problem that severely impacts human health, the environment and economy. Contaminated soil management is process of several steps including the (1) identification and investigation of sites, (2) assessment of potential risks to human and environment, (3) review, selection and planning of possible management strategies, (4) operation of clean-up or pollution control measures and finally (5) close of this measures. This applies to conventional remediation measures for the management of large-scale contaminated sites.

Key words: Polychlorinated Biphenyls (PCBs), Organochlorinated Pesticides (OCPs), Maximum Allowable Concentration (MAC), Oriented Allowable Concentration (OAC), State Hydrometeorological Service (HSH), Republic of Moldova (RM), Persistent Organic Pollutants (POPs), Steppe (St), Reservoir (rz.), River (r.).

1. Introduction

Article 1 of the Stockholm Convention on Persistent Organic Pollutants requires Partiesis to protect human health and the environment from Persistent Organic Pollutants (12 POPs listed in Annex A, B, C - Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene (HCB), Mirex, Toxaphene, Polychlorinated Biphenyls (PCBs), 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane, DDT, Polychlorinated -p-dioxins and dibenzofurans, Hexachlorobenzene).

The Republic of Moldova has recognized and is aware of the problem of chemical hazards, and considers the health and environmental concerns that they pose as a high priority for actions in particular the importance of POPs. The Republic of Moldova signed Stockholm Convention on May 23, 2001 and ratified it on February 19, 2004.

The national policy regarding POPs chemicals is driven by understanding that **national chemical safety management system** needs to be created to prevent degradation and societal, particularly health, impact. Minimization and final elimination of POPs related pressure and impact to the natural and human environment is an integral part of national environmental policy.

1.1. The pesticide background

The Republic of Moldova has never had and does not currently have pesticide producing enterprises or factories, all agrochemicals for plant protection permitted for use in the country have been and are imported from abroad. Pesticides, including POPs, were used in large quantities in the past in Moldova. In the 1950-1990 an estimated total amount of 560,000 tons of pesticides were used in Moldova including 22,000 tons of organochlorinated pesticides (OCPs). Pesticides use registered a peak in 1975-1985 but reduced dramatically over the last 10-12 years (from 38,300 tons in 1984 to some 2,800 tons in year 2000 as active ingredient) *Figure1.*

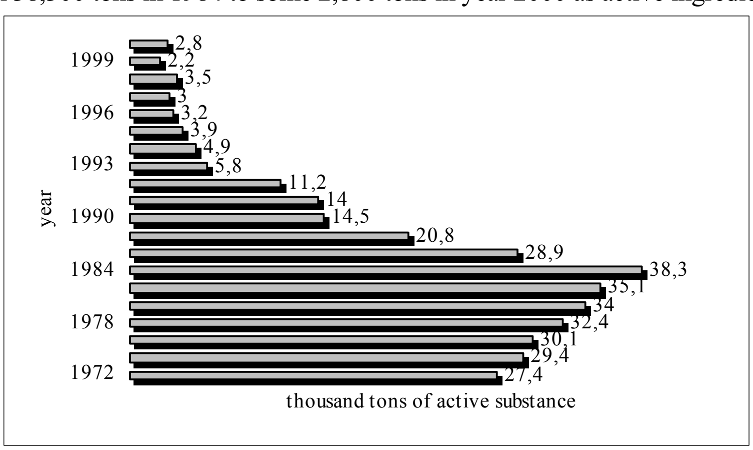

Figure 1. Pesticides use in Republic of Moldova

The absence in the past of controls on pesticides imports, storage and use have resulted in the stockpiling of banned and useless pesticides, and the pesticide dump was built in 1978 in 10 km to the south from the city of Vulcanesti nearly the village Cismichioi in the South of Moldova. Over a period of 10 years (1978-1988) 3940 tons of pesticides were buried there, including 654.1 tons of DDT. Also 1,712 tons of pesticides were stored in 344 warehouses in country site. Nowadays, within GEF/WB "Persistent Organic Pollutants Stockpile Management and Destruction Project the obsolete pesticides were repacked and have been stored in 24 centralized warehouses and over 1150 tones were transported for final disposal.

1.2. The PCBs background

PCBs in Moldova are primarily used in the energy sector as dielectric fluids in power installations, especially transformers and capacitors. The POPs inventory, undertaken in the context of development of national implementation plan (NIP) for POPs, identified approximately 26,300 transformers, 17,000 capacitors and other electro-energy equipment containing a total amount of dielectric oils of approximately 23,900 tons much of which is expected to contain PCBs. The approximate breakdown reported was: capacitors from the electric industry. Most of capacitors were concentrated at the Vulcanesti substation in the south of Republic of Moldova. Actual, within the Project GEF/WB over 900 tones of PCB containing and contaminated capacitors were dismantled and transported for final disposal.

2. Soil POPs Monitoring in RM

According to Monitoring Program the determination of OCPs such as DDTs and HCHs are performed in soil from agricultural areas more than 25 years. Pesticides from stockpiles with obsolete pesticides and oil in energy installation were identified as sources of pollution of soil and other media. Investigation of soil around the stockpiles with obsolete pesticides, soil around pesticide dump and soil around the electric power installations and sediments from main water bodies was included in Monitoring Program of State Hydrometeorological Service later in years 2003-2005.

2.1. Contents of organochlorine pesticides (OCPs)

2.2.1.OCPs contents in Agricultural Soil

Organochlorinated pesticides DDTs, HCHs, lindane have been widely used in the 60-70^th^ years of last century. High persistency, accumulation and global migration to the long distances are the reason for their research in environment. Norm (MAC) of DDTs and HCHs were established and is 0.1mg/kg. The application of DDT was banned in 1970. Activities for measuring of contents of OCPs include DDTs (p-p´DDT, p-p´DDE, p-p´DDD) and HCHs (alpha, beta, gamma-HCH).

Data shows that the largest mean value of HCHs was detected in soil in 1981 with concentration of 0.683 mg/kg (6.83 time exceed norm), and DDTs - in 1983 with concentration of 1.324 mg/kg (13.24 exceed norm). Since 90^th^ years the results have demonstrated the significant decrease of OCPs in soil. During 1992-2005 years findings have shown that the mean contents of DDTs are not high and don't exceed the norm and varies from 0.009 to 0.088 mg/kg, except some particular and isolated cases, (Figure2.). Contents of HCHs in agricultural soils in selected districts during four last years are not higher norm of quality value, maximum concentration is 0,029 mg/kg (0,29 MAC), (Figure3.).

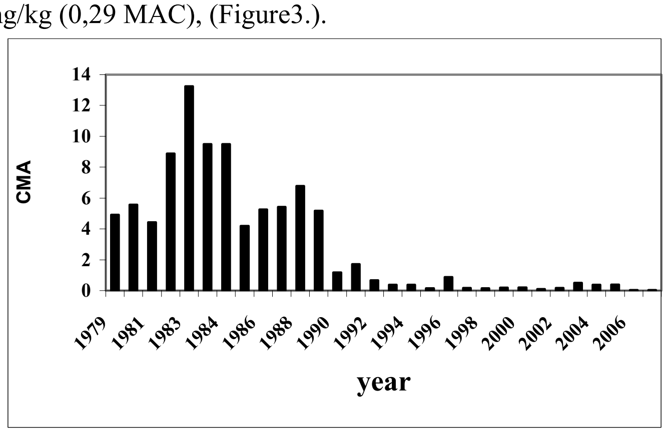

Figure 2. Mean contents of DDTs in agricultural soils of Republic of Moldova

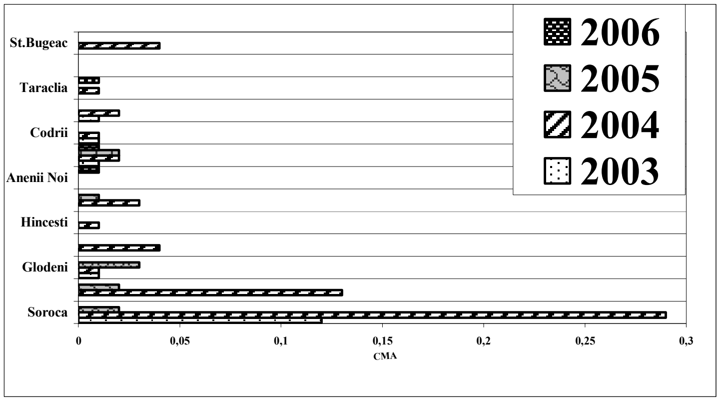

Figure 3. Mean contents of HCHs in agricultural soils from selected districts and background sites

2.2.2. OCPs contents around the warehouses with obsolette pesticides

During years 2003-2006 according the activities of SHS were analyzed 252 soil samples taken around the 21 warehouses were obsolete pesticides have been storied (Figure 10)

In 5 warehouses the contents of HCHs in soil didn't exceed norm of quality value (Figure 4), in 16 warehouses were revealed exceeding of norm of quality value of HCHs. Contents of soil in 13 warehouses varied from 0,130 mg/kg (1,3 MAC) to 1,182 (18,2 MAC), (Figure 6) and the high extreme contamination of soil were revealed in 3 warehouses, ranged between 54 CMA and 116 CMA (Figure 5).

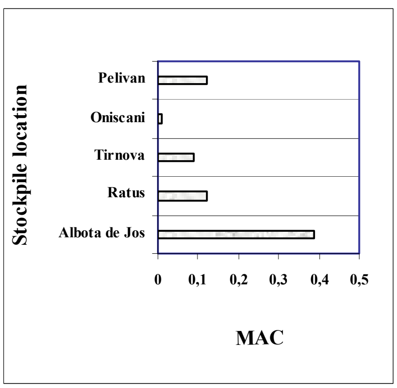

Figure 4. Maximal contents of HCHs in soil around the warehouses

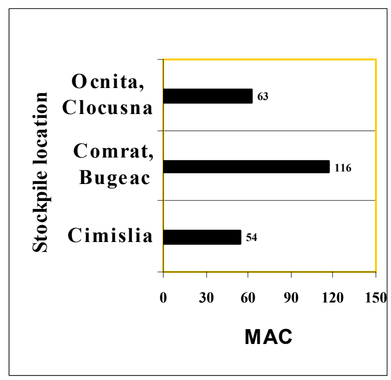

Figure 5. Maximal contents of HCHs in soil around the warehouses

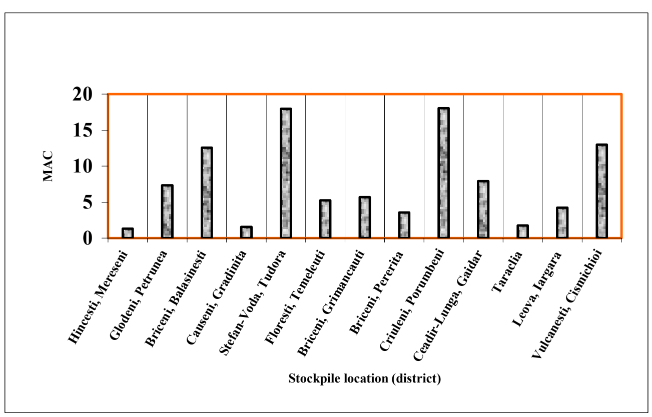

Figure 6. Maximal contents of HCHs in soil around the warehouses

Data shows that in 5 warehouses the contents of DDTs in soil didn't exceed norm of quality value (Figure 7), in 16 warehouses were revealed exceeding of norm of quality value of DDTs. Contents of soil in 10 warehouses varied from 0,170 mg/kg (1,7 MAC) to 1,22 (12,2 MAC), (Figure 8) and the high extreme contamination of soil were revealed in 6 warehouses, ranged between 58 CMA and 1812 CMA (Figure 9).

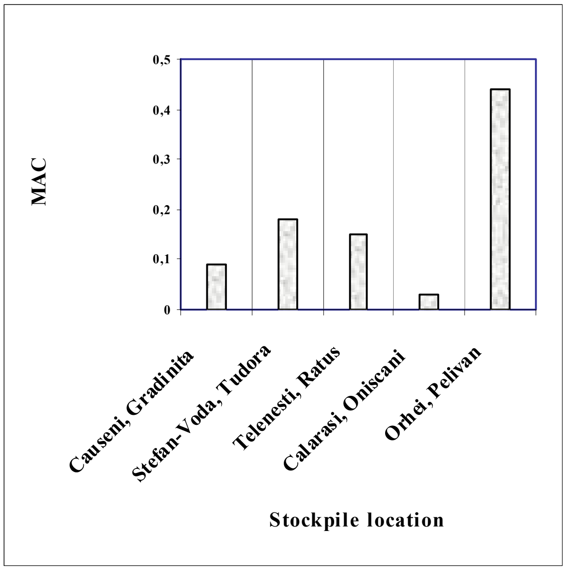

Figure 7. Maximal contents of DDTs in soil around the warehouses

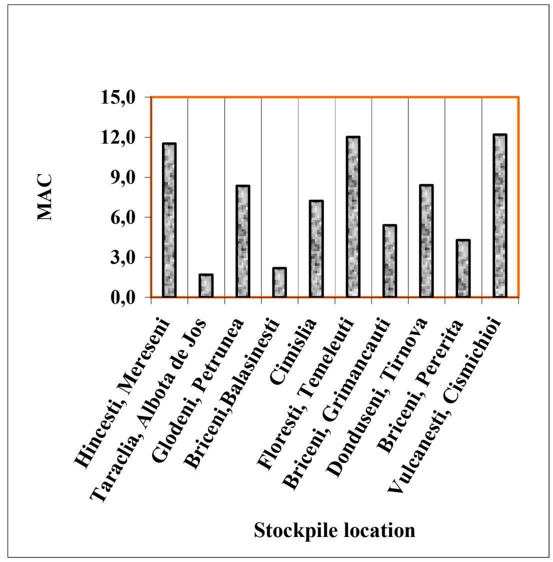

Figure 8. Maximal contents of DDTs in soil around the warehouses

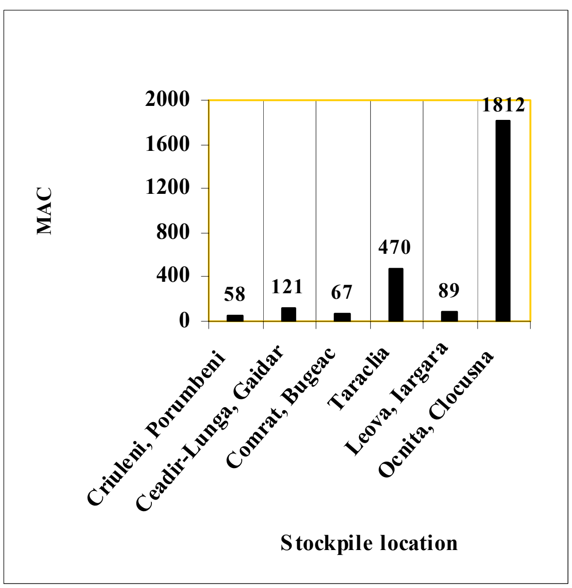

Figure 9. Maximal contents of HCHs in soil around the warehouses

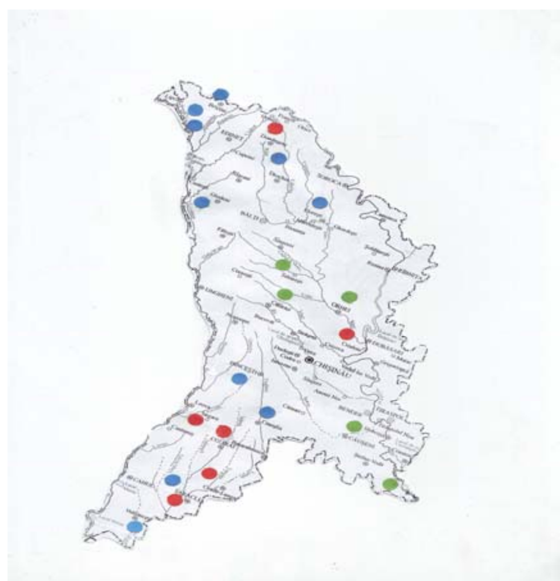

Figure 10. Map location of investigation warehouses

2.2.3. OCPs contents in soil around the pesticide dump in Cismicioi

The absence in the past of controls on pesticides imports, storage and use have resulted in the stockpiling of banned and useless pesticides, and the Pesticide Dump was built in 1978 in 10 km to the south from the city of Vulcanesti nearly the village Cismichioi in the South of Moldova. Over a period of 10 years (1978-1988) 3940 tons of pesticides were buried there, including 654.1 tons of DDT. 14 cells are located there which are well visible from a surface. Twice were carried out the investigations of the Pesticide Dump – in 1997 (within TACIS ENVREG 9705 Project and in 2004. 52 samples of soil and ground were analyzed in year 2004. Organochlorine pesticides DDTs, HCHs HCB were determined in soil samples. The most pollution area was revealed in the territory of Dump between cells up to 178,6 MAC of DDTs, up to 21.2 MAC of HCHs and up to 2,4 Oriented Allowable Concentration of HCB. In samples taken from the west, slope and valley out of Pesticide Dump the values of HCH not exceed quality value, but were revealed the exceeding of DDTs in above mentioned samples up to 5.6 MAC. In total from 52 analyzed samples - 5% samples exceed norm of HCHs and 15% - DDTs. In the sample taken from territory of Dump was revealed exceeding of Oriented Allowable Concentration of HCB with value 2.4. The data shows that no leakage revealed from pesticide dump

2.2.4. PCBs contents in soil in around the energy substations

The PCBs contents were determined in soil in depth 0-10cm around the PCB-containing capacitors in the electrical substations that are in conditions of leakages due to corrosion. During the 2005-2007 years eleven substations were investigated. The results are presented below in Table 1. The norm of PCBs in soil (MAC) is 0.06 mg/kg (Figure 11). Data shows that all investigated area is polluted and the contents of PCBs vary from 0,1 mg/kg with exceeding of norm of quality value 2 times in district Briceni to extreme high content of PCBSs with value 2545,61 mg/kg with exceeding norm of quality value 42427 times in district Donduseni. The results are presented below in Table 1.

Location of Substation	Max. value, mg/kg	Max. value, CMA
Briceni	**2545,61**	**42427**
Orhei	**1958,88**	**32648**
Donduseni	**95,4**	**1590**
Comrat	**63,03**	**1051**
Ungheni	**20**	**333**
CeadirLunga	**7,97**	**133**
Lipcani	**3,52**	**59**
Soroca	**2,55**	**43**
Drochia	**1,1**	**18**
Hincesti	**0,49**	**8**
Straseni	**0,1**	**2**

Table 1. Maximal contents of PCBs in soil in the investigated electrical sub-station

Figure 11. Map location of investigated electrical sub-station

In spring 2005 was carried out the prefeasibility analyses of PCBs in soil in Vulcanesti sub-station. The measurements demonstrate that the soil is contaminated with PCBs. The PCBs in the upper 10 cm varied from 1.3 to 7098 mg/kg. In depth 50-60 cm the concentration ranged from 0.1 to 177 mg/kg. Repeated examination was carried out in September 2006 within "Persistent Organic Stockpile Management and Destruction Project», Task 3 VULCANESTI SUB-STATION, pRE-EXCAVATION AND EQUIPMENT REMOVAL ASSESSMENT. The results show that all area is contaminated with PCBs.

2.3.OCPs and PCBs contents in sediments

Survey of contents of OCPs in sediments was included in Monitoring Program of SHS in 2003. Monitoring of sediments includs11 sampling sites established in main water bodies of Republic of Moldova (6 reservoirs, one lake and two rivers). As a result the most samples contained organic compounds. DDTs concentrations vary from 0.5 to 12.9 mkg/kg, HCHs concentration - from 0.2 to 0.6 mkg/kg, PCBs contents vary from 0.3 to 15.8 mkg/kg. Data shows that agricultural and industrial activities caused contamination of sediments with Persistent Organic Pollutants. As expected, the POPs were retained in sediments, indicating its adsorption in sediment organic matter.

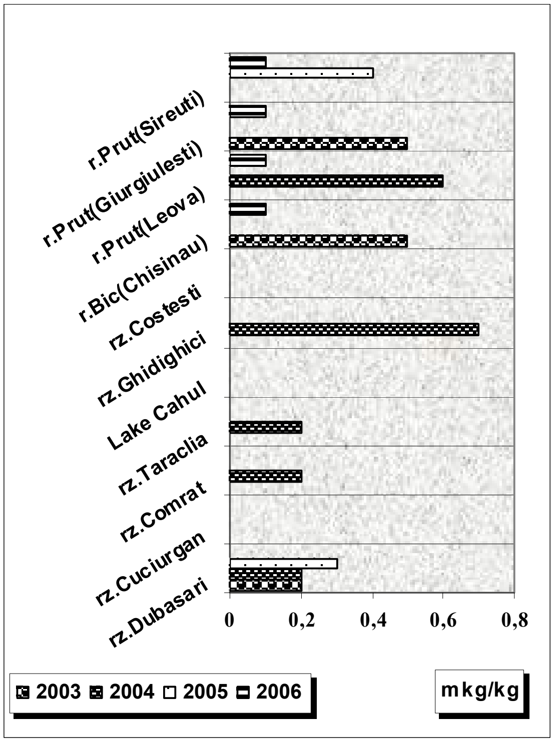

Figure 12. Maximal contents of HCHs in sediments

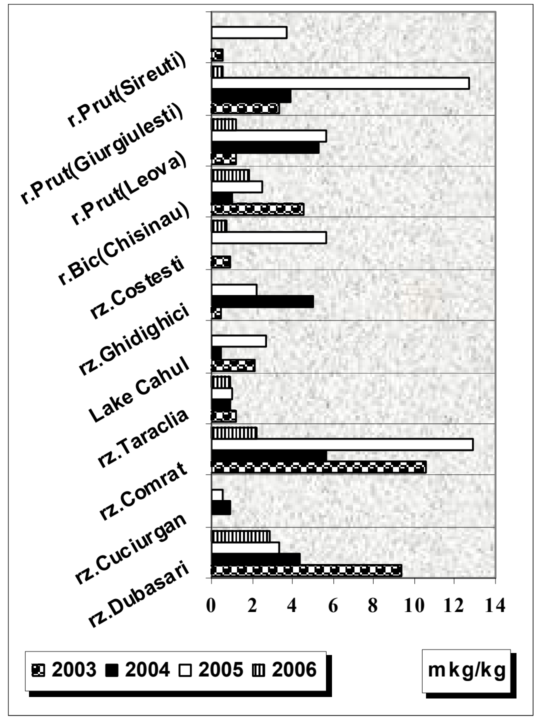

Figure 13. Maximal contents of DDTs in sediments

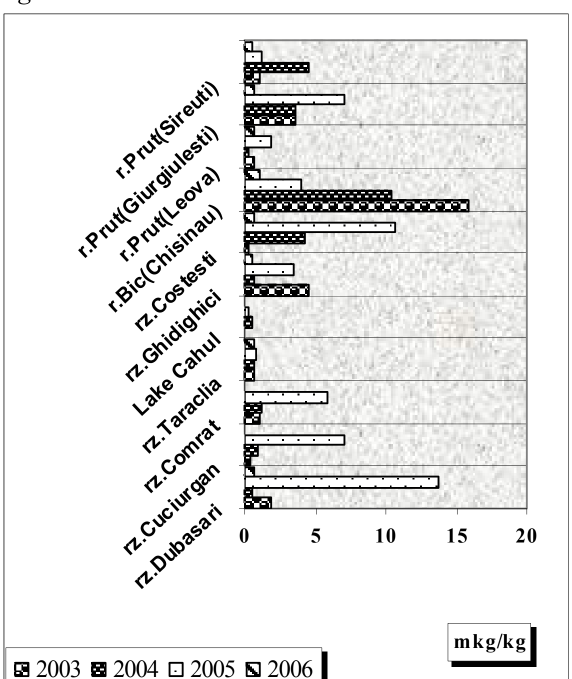

Figure 14. Maximal contents of PCBs in sediments

Figure 15. Map of location of investigated sediments

Conclusion

- Contents of DDTs and HCHs in agricultural soil continue to decrease.
- Soils around the stockpiles with obsolete pesticides are polluted and need the application of remediation technologies.
- Soil around the power energy installations contaminated with PCBs has different pollution and needs various remediation technologies.
- Above mentioned contaminated sites and many others places are danger to the environment that is to be taken into consideration in the course of further investigations.
- All sediments data shows the dissemination of POPs as a result of historical use, industrial activities and atmospheric deposition.

References:

1. Stockholm Convention on Persistent Organic Pollutants (POPs), p.4, p.33-40.
2. National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants Republic of Moldova CHISINAU, Stiinta, 2004, p.44, p.49.
3. G.Victor Buxton, M.Sc.,P.Eng. Hazatdous Chemicals International Consultant Ottawa, Ontario, Canada, STAR Roster Reviewer Comments, May 21,2005, Moldova Persistent Organic Pollutants (POPs) Stockpiles Management and Destruction Project, Project Document, October 2005, Report No:33862-MD.
4. Persistent Organic Pollutants (POPs) Stockpiles Management and Destruction Project, Project Document, October 2005, Report No: 33862-MD. P.32-33.
5. U.S. McKnight, M.Finkel. Estimation of required natural and enhanced attention as part of early decision-making in contaminated land management.
6. Valentin Plesca, Anatol Gobjila, Ion Barabarasa, Larisa Cupcea. The GEF/WB “Persistent Organic Pollutants Stockpile Management and Destruction Project.

MICROBIOLOGICAL CHARACTERISTIC OF PESTICIDE POLLUTED SOILS

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Pesticide contamination can impact soil ecosystems sufficiently to result in significant losses in soil quality and environment. The negative impact of pesticides results from their toxicity to processes, catalyzed by soil microorganisms. The soil microbial community could serve as an indicator of losses in soil quality due to pesticide contamination and as measure of reclamation progress and success. At present indices of activity, biomass and diversity of soil microbial community are suggested for the estimation of soil quality [2 - 4] as well as for the stability of agricultural and natural ecosystems in conditions of the anthropogenic impact [1]. The biotechnology is an important approach for the detoxification of polluted sites by toxic organic pollutants [5]. The actual situation with microbial communities is important for the better understanding of detoxification processes.

The objective of this investigation was the evaluation of soil microbiological status as an indicator of the impact of old pesticide contamination and subsequent phytoremediation management procedure used at a field site.

Materials and methods

The experimental site is located in the central region of the Republic of Moldova in Hincesti district near the old chemical storage "Balceana". Soils were contaminated by HCHs and DDTs. The large interval of the pesticide concentration was obtained at investigated site: HCHs from 10,0 to 1595,0 μg/kg; DDTs from 38,8 to 4268,1 μg/kg. Soil samples of 0-20 cm layer were collected from 2 plots, before and after planting phyto-remediation experiment on this site (Fig 1). Sampling was carried out in May and September of 2007. All soil samples were sieved to 3 mm and maintained at 4^0C.

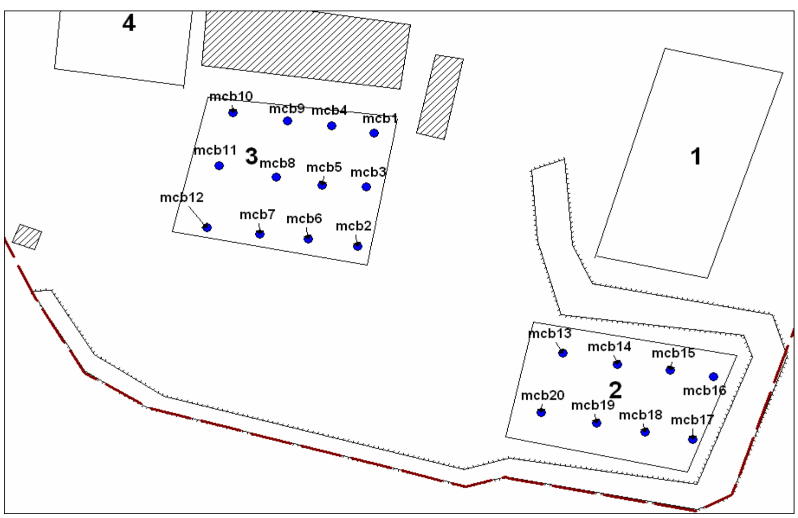


Figure 1. Sampling plan for soil microbiology investigation

Microbial biomass C (C_{MB}) was measured by the rehydratation method based on the difference between C extracted with 0,5 M K_2SO_4 from dried soil at 65-70^0C for 24 h and fresh soil samples using K_c coefficient of 0,25 (6). K_2SO_4 – extractable organic C concentrations in the dried and fresh soil samples were simultane-ously measured using dichromate oxidation. The quantity of K_2SO_4 – extractable C was determined at 590 nm with "Specol-221" spectrophotometer (Germany).

Counts of culturable microorganisms (bacteria, actinomycetes and fungi) were obtained on agar plates [7,8]. Ammonificators were cultivated in peptone medium, nitrogen assimilating bacteria and actinomycetes

- in amylaceous ammoniacal medium. Fungi were counted using Czapek agar medium. Plates were incubated at 28^0C in darkness. All values for microbiological variables were determined by three repetitions.

Results and discussion

*Before phytoremediation***.** Old pesticide polluted soils showed a significant fluctuation in the microbiological indices (Table 1 and fig. 2). The microbial biomass content before the realization of phytoremediation procedure ranged between 159,6 - 325,4 μg C g^{-1} soil (plot 3) and 31,8 – 271,0 μg C g^{-1} soil (plot 2). The variation coefficient was estimated to 23,2-52,3%. The relative changes in the counts of culturable bacteria, actinomycetes and fungi suggest that the soil microbiological status may be resulting in differences in levels of the contamination by pesticides.

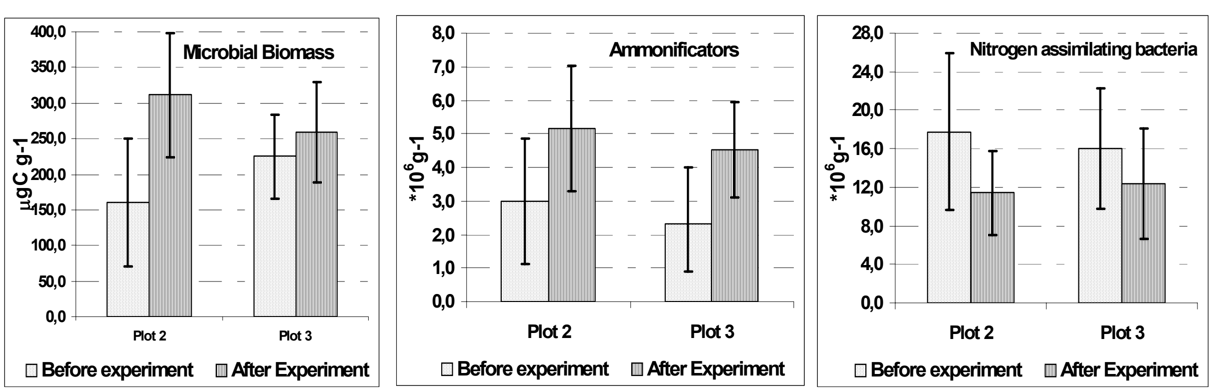
Pesticides contamination also resulted in changes in the structure of the soil microbial community, in particularly, soil fungi. This difference can be observed by the example of 11 and 19 samples (fig 3). Pesticides contamination is the anthropogenic factor for the selection of resistant species of microorganisms. The dominant bacteria culture was selected from plot 3, which can be an indicator for old pesticide polluted soils.

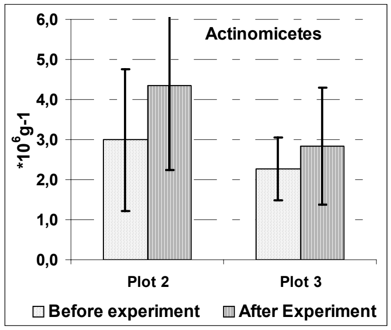
Microbial community indices of pesticides polluted soils before and after the phytoremediation experiment

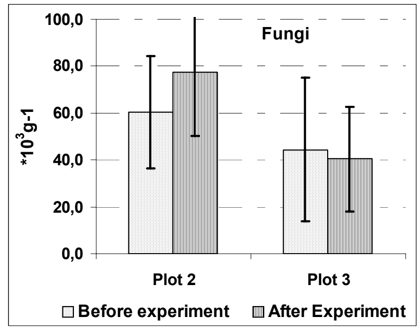
Table 1

C_{MB}	Viable counts of microorganisms				C_{MB}	Viable counts of microorganisms			
	ammonificators	nitrogen assimilating bacteria	actinomycetes	fungi		ammonificators	nitrogen assimilating bacteria	actinomycetes	fungi
□gC g^{-1}	$*10^6g^{-1}$	$*10^6g^{-1}$	$*10^6g^{-1}$	$*10^3g^{-1}$	□gC g^{-1}	$*10^6g^{-1}$	$*10^6g^{-1}$	$*10^6g^{-1}$	$*10^3g^{-1}$
Plot 2									
Before experiment (Average/St.dev)					After experiment (Average/St.dev)				
160,3	3,0	17,8	3,0	60,5	311,4	5,2	11,4	4,4	77,5
90,5	1,9	8,2	1,8	23,8	87,2	1,9	4,4	2,1	27,5
Plot 3									
Before experiment (Average/St.dev)					After experiment (Average/St.dev)				
225,4	2,3	16,0	2,3	44,4	259,2	4,5	12,4	2,8	40,5
59,0	1,7	6,3	0,8	30,7	70,8	1,4	5,7	1,5	22,4

Figure 2. Soil microbiological characteristics for two investigated plots before and after phytoremediation experiment







The zonal microbiological soil parameters for "chernozem" are in the following relation with the investigated site: microbial biomass **281,3**/225,4 – 160,3 µgC g^{-1} (bold – zonal "chernozem"/ plot 3 – plot 2); amonificators **3,2**/2,3 – 3,0; nitrogen assimilating bacteria **14,3**/16,0 – 17,8; actinomycetes **3,1**/2,3 – 3,0; fungi **32,6**/44,4 – 60,5. The total microbial biomass is decreased essential on polluted sites in the comparison with the regional value. Fungi and nitrogen assimilating bacteria are increased on the contrary. Other parameters are in the close interval.

*After phytoremediation***.** The phytoremediation method is one of the main soil management practices, which promotes the natural reclamation of pesticide polluted soil by stimulation of microorganism activity. The incorporation of root exudates and plant residues into the soil results in the intensification of microbiological processes. The phytoremediation procedure of pesticide polluted soils, used at the site, exerts essential impact on the soil microbial community from two contaminated plots. According to statistical parameters the content of soil microbial biomass increases from 197,5-240,5 to 248,1-270,3 µgC g^{-1} for plot 3 and from 117,4-208,0 to 264,2-358,6 µgC g^{-1} for plot 2. The similar trend was evident in viable microbial population size (ammonificators and actinomycetes). There were no clear differences in fungi quantity between period before and after phytoremediation. However, the tendency towards stimulation of soil fungi at the plot 2 was observed.

The phytoremediation procedure led to decreases in variability of microbiological indices. Variation coefficient ranged from 23,2% to 72,1% for plot 3 and from 37,8% to 52,3% for plot 2 before phytoremediation experiments. Variation coefficients were estimated to 10,2-53,9% for plot 3 and 28,5-46,1% for plot 2 after phytoremediation experiments accordingly. This result indicates that the phytoremediation method provides the formation of soil continuum more homogeneous then in contaminated soils due to the interaction between soil microorganisms and plants.

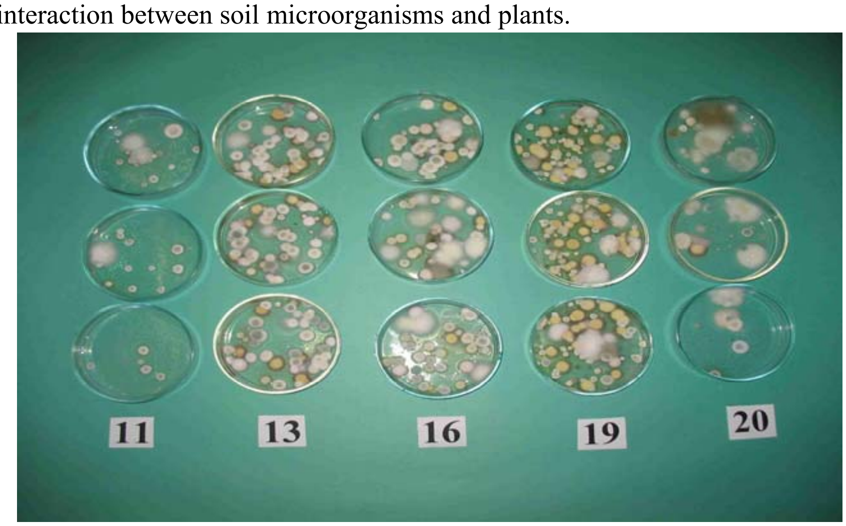


Figure 3. Fungi diversity in DDTs contamination soils:
mcb11, mcb13, mcb16, mcb19, mcb20

Thus, the data suggest that even in the most extremely pesticide-stressed sites, adequate microbial populations exist to support remediation efforts. Adaptation of soil microorganisms to high pesticide levels provides the recovery of the soil ecosystem at these sites.

Conclusions

Old pesticide contaminated soils characterize by high variability of microbiological indices and a lower microbial biomass value and viable population size than the optimum level, providing the soil system stability. Phytoremediation experiments have a positive effect on the soil microbial communities. Improvements in the microbial community with phytoremediation most likely have result in a decrease of pesticide total content and its toxicity. Microbial parameters may be useful in the characteristic of the reclamation progress in highly contaminated soils.

References:

1. Doran J.W., Liebig M., Santano D.P. (1998) Soil health and global sustainability: Paper presented at 16^{th} World Congress of Soil Science, 20 – 26 Aug., 198. – Montpellier, France,. - 7p.
2. Kennedy A. C., Papendick R.I. (1995) Microbial characteristics of soil quality. J. Soil and Water Conserv., 50, nr 3, pp. 243 – 248.
3. Lupwayi N.Z., Harker K.M., Clayton G.W. and others (2004) Soil microbial biomass and diversity after herbicide application. Canadian J. Plant Science, V84, nr. 2, pp. 677 – 685.
4. Lützow M., Leifeld J., Kainz M., Kögel – Knabner I., Munch J.C. (2002) Indications for soil organic matter quality in soils under different management. Geoderma. 105, nr 3-4, pp 243 – 258.
5. DANG Thi Cam Ha, et al (2007) Application of bioremediation technology for detoxification herbicide/dioxin of contaminants in soil. 9th International Forum of HCH and Pesticides, Chisinau.
6. Благодатский С.А., Благодатская Е.В., Горбенко А.Ю., Паников Н.С. Регидратационный метод определения биомассы микроорганизмов в почве // Почвоведение, 1987. - №4. – С.64-71.
7. Йожеф Сэги. Методы почвенной микробиологии. – М.: Колос, 1983. – 295 с.
8. Методы почвенной микробиологии и биохимии. Под ред. Д.Г.Звягинцева. – М.: МГУ, 1991. – 224 с.

POPs NIP AND THE ESTABLISHMENT OF BIOMONITORING OF CHEMICALS IN THE REPUBLIC OF SLOVENIA

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In preparation of the National Implementation Plan (NIP) for POPs Slovenia used the NIP Guidance and Dioxin inventory Toolkit. Additionally Action Plan Preparation Guide and The Guide for Socio-economic Assessment have been consulted. The multi-stakeholders were very well presented through the Slovene Chamber of Commerce. As little interest to the participation in the project has been expressed from the stakeholders and as there is no direct production of POPs, no stakeholder was directly involved. We present a short review of the NIP. The two step procedure - A: Inventory and B: Action plan development - was appropriate approach for us. The benefit is the detailed POPs inventory documentation on the POPs chemicals as well as the research done. Under the sub-project important activities have been initiated besides the proposed action plans (public education and awareness-raising). The role of governmental and professional institutions in the POPs management was determined. The review of the research programmes on specific polluted areas was prepared and the socio-economic aspects of POPs management, too. As an additional result of all this action the tentative programme of bio-monitoring was prepared and performed for the first time in the year 2005. Human milk and blood and few samples of two wildlife species were sampled and analysed on many parameters as POPs and PTSs (PCB, PCDD/F, pesticides, metals, benzene, fluoride). Because of the small extent of the sampling only few data were acquired. Based on these experiences we established a long-term biomonitoring programme to gather more data on the exposure of the general population of Slovenia to these chemicals, with the establishment of the national reference values for each measured parameter.

Key words: POPs, bio-monitoring, human milk, human blood, wildlife species.

Introduction

The Stockholm Convention on Persistent Organic Pollutants (the Convention) is a global environmental protection treaty for the purpose of protecting human health and the environment from the adverse effects of persistent organic pollutants. The Convention was established on 22nd May 2001. Republic of Slovenia acceded to the Stockholm Convention on Persistent Organic Pollutants on 23rd June 2001 and ratified it on 4th May 2004.

The project of the National implementation plan (NIP) was conducted by the National Chemicals Bureau at the Ministry of Health of the Republic of Slovenia with the financial assistance of GEF/UNEP. Representatives from different administrative authorities, experts in the fields of chemistry, ecology, medicine and agriculture and also the representatives of non-governmental organizations - all participated in the project, with regard to expert content of the tasks. All of the available information on the production, use, import and export of twelve chemical compounds treated in the Convention was gathered and evaluated within the framework of the NIP project. The examination of technical capacities and adequacy of a monitoring programme was performed on the basis of data on POPs, which offered information on the level of pollution with POPs in the environment and food, and on their effects on human health. It contains the strategy and the action plan with proposal of priorities regarding the implementation of the NIP in short-term and long-term periods.

NATIONAL IMPLEMENTATION PLAN ON MANAGEMENT OF POPs:

Strategy and elements of an Action plan

Data on the past production and use of all of the twelve POPs substances and data on the level of environmental pollution were gathered within the framework of the project. Data on the present situation of environmental pollution with POPs compose the basis for the planning of subsequent activities for environmental protection and protection of health of the residents of the Republic of Slovenia. Much like in other EU countries, numerous activities for the protection of the environment from POPs substances are being carried out in the Republic of Slovenia, too. Main sources of emissions are being removed according to plans, what already results in lower levels of POPs substances in the environment.

Regarding the present situation, the priorities of the Republic of Slovenia for the protection of the environment and human health from POPs substances are:

- preparing measures for the reduction of exposure to PCB of the population from the region of river Krupa;
- strengthening the implementation of legislation in the area of POPs;
- further reduction of POPs emissions in the environment,;

- research on the effects of POPs on human health;
- research on the burden of population with POPs and the definition of a relationship between dose and effect;
- setting up the central information system for POPs in the Republic of Slovenia;
- educating the population about POPs and their effects on the environment and human health;
- joining the international activities from the area of POPs.

Strategic objectives from different areas of environment and health protection are designated on the basis of chosen priorities of the Republic of Slovenia for the protection of environment and human health from POPs substances. Action Plan for taking measures is prepared for each area as it is presented in table 1.

Strategic objectives and action plan of measures for meeting these objectives

Table 1

Method of protection	Strategic objective	Action Plan
Regulation by law of the management of POPs substances & implementation of supervision	• Establishment of the inter-ministerial sub-commission for POPs • Implementation of Slovene legislation according to the EU legislation and the requirements of the SC Treaty	• Institutional and legislative strengthening in the area of POPs
Determination of the extent of exposure to the POPs in the Republic of Slovenia	• Survey of the burden and the levels of POPs substances in the environment	• Sources of POPs in the Republic of Slovenia identified and documented in the NIP (realized)
Prevention and reduction of exposure of the population to POPs in the environment	• Collected data on old environmental burdens from the packaging, use and incorrect disposal of POPs pesticides in the past; preparation of plan for the remediation of these burdens • Prepared strategy for the final annihilation of a landfill for waste materials containing PCB • Inventory of the emission sources and emissions of PCDD/PCDF • Use of alternative chemicals that are harmless to the environment and health • Protection from ecological burdens in the environment • Use of BAT/BEP in the planning of new industrial technologies • Prepared strategy for the extension of POPs list • Protection of women in the reproductive period from exposure to POPs substances at the workplace	• Production, market circulation, use, stock of and wastes from plant protection products containing POPs • Production, import, export, use, identification, labelling, removal, storage and disposal of PCB and equipment with PCB content • Production, market circulation, use, stock of and waste materials containing DDT • Inventory, supervision and restriction of the unintentionally produced PCDD/F, HCB and PCB • Identification of stock, products in use and waste for pesticides, DDT, HCB • Identification of contaminated areas and appropriate action
Monitoring the levels and studying the effects of POPs on human health	• Monitoring and studying the levels of POPs in population with emphasis on the population of region of the town Semič and river Krupa, specially on women in fertile period and on occupationally exposed workers • Following and studying the effects of POPs on human health	• Research and development strategy
Gathering, processing and forwarding data on POPs in the Republic of Slovenia	• Systemic gathering of data for the evaluation of environmental burden and the effects on human health in representative areas – supplementation of the POPs monitoring programme in accordance with the requirements of the Stockholm Convention • Setting up the information centre for POPs	• Data exchange strategy • Reporting • Monitoring of POPs in the Republic of Slovenia
Public information, aware-	• Awareness raising in general public	• Public awareness, notification and

ness raising and education	• Informing governmental policy makers, the media, and experts in the field of environment about the effects of POPs on human health • Education of doctors and medical professionals about the effects of POPs on human health • Informing the industrial sector about the adverse effects of POPs	education
Joining the international activities from the area of POPs	• Participation in harmonised international research • Participation in activities of the World Health Organization • Offering the support to the developing and transitional countries in their preparation of NIPs on POPs	• Research and development strategy

Planned measures shall provide the reduction of exposure of the population to the POPs substances and healthier living environment in accordance with the recommendations from the Stockholm Convention.

The main necessity of Slovenia in the area of POPs substances is the examination of the burden of human population with PCB and dioxins/furans. The inventory showed that the average levels of PCB and dioxins/furans in different tissues are unknown in Slovenia, even the most essential ones necessary for international comparison - the burdens of mother's milk. The attention should be paid to the vulnerability of the youngest population and to the planning of possible special measures for their health protection, which is the main objective of the Convention. The research and its periodic updating should enable determination of the present condition and trends of these burdens, as well as the preparation of appropriate recommendations.

Short-term and Medium-term Measures

2. Determination of the existing situation and subsequent periodic monitoring of levels of PCB and dioxins/furans in mother's milk. A selection of adequate recommendations.

The programme "Monitoring of chemicals in organisms" proposed within the framework of NIP includes, in addition to heavy metals, a survey of the presence of POPs substances in human blood and human milk samples and in tissues of wild animals chosen as indicators.

Measurements of PCBs shall be undertaken from mother's milk and blood in the selected regions of Slovenia at first. These data will: (1) determine the national reference values, (2) demonstrate the wider burden of Slovene population with these substances and (3) enable to compare the results with other regions and countries.

3. Integration into international movements for the evaluation of trans-boundary emission of POPs substances and determination of Slovenian contribution to the long-range pollution.

Long-term Measures

1. Scientific research of the relation between the exposure to POPs substances and health condition of different population groups, gender and age.
2. Research of maternal exposure to POPs substances before and during pregnancy and their effect on development of foetus and child.
3. Research in the field of new scientific information and methods of toxicology (genomics, proteomics) for understanding mechanisms of toxic agency of POPs substances.
4. Development of appropriate indicators of exposure to specific POPs substances in the environment and the use of these indicators for monitoring effectiveness of measures for protecting human health from POPs substances in the environment.

ESTABLISHMENT OF THE NATIONAL BIOMONITORING OF CHEMICALS

Due to improper disposal of equipment and substances containing PCBs in the region of Semič in the eighties we have many of the problems still to solve (Jan and Tratnik, 1988). As a result of NIP the research of the burden in the residents, in local environment (soil, sediment, water and air) and in locally produced food with

PCBs and dioxins/furans should be continued. In addition the appropriate research has to be undertaken, which shall determine also the Slovene contribution to pollution over large distances with these substances.

The beginning was modest: bio-monitoring of three tissue samples of the adipose tissue of the brown bear was successfully carried out in 2004. Slovenia is one of the sparse European countries with preserved viable indigenous brown bear (*Ursus arctos*) population. On account of this exceptional opportunity of Slovenia - the abundant presence of this animal species, as well as adequate expertise and analytical equipment, a tentative research was carried out regarding the presence of dioxins and PCBs in tissue samples of the brown bear (*Ursus arctos*) (Bolta et al, 2004). In addition in 2005 few tissue samples were taken from the hare (*Lepus europaeus*) and the boar (*Sus scrofa*) and also of the human blood and milk (Program …, 2006). The preliminary results demonstrated the right of the decision for such environmental bio-monitoring. With continuation of this research Slovenia could contribute to the global knowledge about tissue burden with dioxins and PCBs in some wildlife species as environmental indicators and in human population as well.

The task of "Monitoring of chemicals in organisms" is the beginning of a long-term programme, establishing in the period of 2007-2009. Its aim is to determine the exposure to chemicals with an ascertainment of the sources and trends in time by the geographical regions and the establishment of the national reference values. The reference (background) values are statistically counted up and mean the 95-percentile at the 0,95 confidence interval for the measured parameter in chosen population (Christensen, 1995; Wilhelm et al., 2003).

In accordance to the UNEP and WHO Guidelines (WHO, 2007), The European Environment & Health Action Plan (CEC, 2004) and the national Act on chemicals (Act …, 2003) the study will establish the basis of the monitoring of chemicals in organisms (bio-monitoring) in Slovenia. The results will enable accurate scientific evaluation of the environmental exposure to chemicals in selected regions of Slovenia and in the country as whole for the population of adults of both gender of age from 20 to 35 and also for breastfed children from 2 to 8 weeks old.

At least three selected wildlife species will be evaluated. At the selection of species it is necessary to consider the principles of sustainable use and conservation of the nature and the endangered species not to affect their natural populations.

For both, human and animal samples it is provided sufficient number of samples to assure the statistical power of the results.

For the selection of parameters for monitoring (presented in Table 2) we considered:

- guidelines of the European Commission and the European Environmental Agency (CEC, 2004; EEA, 2005);
- guidelines of the World Health Organisation (IPCS, 2004; WHO, 2007);
- priority list of the Agency for Toxic Substances and Disease Register (ATSDR), includes 275 chemicals, used as basis of bio-monitoring in the USA (CERCLA, 2007);
- data from former studies in Slovenia.

Selection of chemicals for monitoring that can significantly contribute to the burden of dangerous substances in the environment of Slovenia

Table 2

PBDE - polybrominated diphenyl ethers
PCB - standard and other polychlorinated biphenyls and chlorinated organic pesticides
PCDD/Fs - Polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzo-furans (PCDD/Fs) (dioxins/furans), PCBs similar to dioxins
Cd and its compounds
Hg and its compounds
Pb and its compounds
Benzene
Fluorides

Bio-monitoring is a good tool for the evaluation of exposure to the pollutants via environment. Data produced by the bio-monitoring are not dependent on the path of exposure to the specific chemical (Pirkle et al., 1995), but they show the cumulative exposure to this chemical. By elaborate plan of gathering and analysing the series of biological samples we will acquire the data on changes and trends of exposure in a time period. In addition, the data on living habits of the examinees and on their former exposure to the chemicals (e.g. hobbies, personal habits, diet, vocation) gathered from the polling based on elaborate questionnaire will enable the identification of the most important sources and paths of exposure.

The results would be: more accurate exposure assessment, qualitative improvement of the risk assessment and planning of the right measures for risk reduction regarding the exposure to chemicals, especially for the POPs.

References:

1. Act on Chemicals. Official Journal of the Republic of Slovenia, No. 110/2003 (12.11.2003).
2. Bolta Ž, Križanec A, Vončina E, Cencič Kodba Z, Jonozovič M. Dioxins and PCBs in the adipose tissue of Slovenian brown bear. 9th International Conference on Life Sciences & 1st International Congres on Toxicology, Nova Gorica, Slovenia, September 18-22, 2004; 169.
3. CEC (Commission of the European Communities). Communication from the Commission to the council, the European Parlament, the European Economic and Social Committee. »The European Environment & Health Action Plan 2004-2010. Brussels, 9.6.2004.
4. CERCLA Priority list of hazardous substances. http://www.atsdr.cdc.gov/cercla/05list.html (17.05.2007)
5. Christensen JM. Human exposure to toxic metals: factors influencing interpretation of biomonitoring results. Sci Total Environ. 166:89-135 (1995).
6. EEA (European Environment Agency), European Commission . Directorate General. Joint Research Centre. Environment and Health. Report No 10/2005, Kopenhagen.
7. http://www.chem.unep.ch/pops/
8. IPCS (International Programme on Chemical Safety). Project on the Harmonization of approaches to the Assessment of Risk from Exposure to Chemicals. WHO, Geneva, 2004.
9. Jan J and Tratnik M. Polychlorinated Biphenyls in Residents around the River Krupa, Slovenia, Yugoslavia. Bull Environ Contam Toxicol,1988; 41: 809-14.
10. Pirkle JL, Needham LL, Sexton K. Improving exposure assessment by monitoring human tissues for toxic chemicals. J Expo Anal Environ Epidemiol 5: 405-424 (1995)
11. Program monitoringa kemikalij v organizmih 2007-2009. URSK (Urad Republike Slovenije za kemikalije), Ministrstvo za zdravje, Ljubljana, 2006.
12. Resolution on the National programme for management of persistent organic pollutants. National Chemicals Bureau, Ministry of Health of the republic of Slovenia. 2007; in parlamentary procedure.
13. Wilhelm M, Ewers U, Schultz C. Revised and new reference values for some persistent organic pollutants (Pops) in blood for human biomonitoring in environmental medicine. Int J Hyg Environ Health 206: 223-229 (2003).
14. WHO (World Health Organisation). Guidelines for Developing a National Protocol. Fourth WHO-Coordinated Survey of Human Milk for Persistent Organic Pollutants in Cooperation with UNEP. Geneva, 2007.

ORGANOCLORIDE PESTICIDES IN FOOD AND BREAST MILK: PAST AND PRESENT SITUATION IN BELARUS (REVIEW)

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In Republic of Belarus state sanitary inspection authorities and scientific centers of Ministry of health have monitored the concentration of organochloride pesticides (OCP) in soil, drinking water, food and biological samples (breast milk and adipose tissue) for quite a long time, since 60s, when the use of this pesticides was allowed in Belarus.

Over 37 thousand tests for DDT, hexachloran and other chlorine-containing pesticides were conducted in Belarus between 1967 and 1971. The percentage of contamination of food products by organochloride pesticides is 13.4 – 3.8 % (in 1967 and 1971 respectively) including in excess of the maximum permissible concentration – 7.8 and 2.1 % [1]. The highest concentration of pesticides residues was detected in potatoes that can be explained by extensive use of DDT against Colorado beetles. In 10% of samples the detected concentration exceeded the maximum permissible concentration. The excess of the maximum permissible concentration was registered in other vegetables, milk (associated with fodder contamination and use of organochloride pesticides (aldrin, DDT and hexachlorane) in veterinary practice), and eggs.

At present food product are tested mainly for DDT, its metabolites and HCCH [2] . Around 30 thousand analysis for organochloride pesticides are made around the country in every region. For example, in 2004 the laboratories of the sanitary inspection authorities tested 32 760 samples of which 17 failed to meet the sanitary norms and requirements. Analysis of pesticides residues in food, that potentially gives the main doses for population (meat, fish, milk, eggs) shows, that in spite of percentage of organochlorine pesticides residues detection is low there are cases of detection of rather high concentration (1/2 of maximum permissible concentration (MPC)).

The analysis of the data on monitoring of the residual content of chlororganic pesticides conducted by the sanitary inspection authorities **can be summarized as follows**:

- during the surveyed period (over 30 years) both the concentration and percentage of detection of pesticides classified as POPs in food products decreased dramatically;
- detection of DDT and HCCH tends to prevail in the Brest region; aldrin and heptachlor – in the Vitebsk region: DDT – in the Gomel and DDT and hexachlorbenzole – in the Grodno region;
- percentage of detection of pesticides in amount higher than MPC vary across regions (ranging from 0 in Minsk and Vitebsk region to 2.1 % in Grodno region;
- the highest percentage of detection of pesticides classified as POPs in surface water and soil (up to 75% of detection) has been recorded in Vitebsk region because the samples were taken off close to obsolete pesticides landfilled.

The special investigations were made to analyze the quantity of residues of organochloride pesticides in domestic food product (in Mogilev and Gomel region) and products that are imported [3,4+].

The survey to analyze the domestic product covered the locally produced food including bread (rye-bread and white bread), milk, meat (beef, pork, chicken) and vegetables (potatoes and sugar-beet). Certain concentration of OCP including aldrin, HCCH, and its isomers (α, β and γ) heptachlor, DDT and its metabolites (DDD and DDE) have been identified. Heptachlor, aldrin and DDT have not been detected in tested food products. There are food products which virtually do not contain OCP, for example apples (4 samples have been analyzed), sugar-beets (1 out of 11 samples contained DDE in the amount of 0.03 μg/kg) potatoes (6 out of 11 samples contained DDE in concentration 0.03-0.1 μg/kg). 4 samples of drinking water out of 7 were contaminated by DDE less that 0.01 μg/l. The concentration of DDE in carrots and cabbage was 0.05-0.2 μg/kg and 0.001-0.1 μg/kg respectively. The highest concentration of DDE in vegetable origin products was registered in rye-bread and white bread (0.06-0.15 μg/kg). Dairy products contain DDE and α, β and γ-isomers of HCCH; the concentration of α- and γ-isomers was 0.03-0.2 and β-isomers – 0.1-0.7 μg/kg. As a rule, milk samples contained one of monitored isomers. DDE residues were detected in milk in concentration

0.05-0.3 μg/l. the concentration of OCP pesticides in fat-rich products was a bit higher what can be explained by nature of POPs pesticides. The concentration of DDE ranged from 0.3 to 0.8 μg/kg and from 0.1 to 2.5 μg/kg in sour cream and butter respectively. Unlike milk two or more isomers were simultaneously detected in butter. Small amount of DDE (0.05-4 μg/kg, 1.5-3.0 μg/kg and 0.1-1.5 μg/kg respectively) as well as residues if HCCH isomers were detected in chicken, beef and pork. 9 samples of eggs were tested. DDE and HCCH isomers were detected in all samples (the concentration ranged from 0.1 to 1.0 μg/kg). The monitoring of changes of concentration of the OCP residues in food products (within 3-5 years) has demonstrated that both the number of detection and the content of OCP tend to reduce.

It can be concluded that:

- DDE residues have been registered in almost 100% of the tested samples and food products;
- the percentage of detection of HCCH isomers is 28%;
- no residues of aldrin, DDN and heptachlor have been registered in the samples;
- the detected concentration is considerably lower that the permissible level; however, in some samples the concentration of DDE residues reaches the permissible level and there are also of other OCP;
- food product of vegetable origin contain less residues of OCP that fat-rich food products.

The above referred data give an idea of contamination of domestically produced food with OCP. However, given the expansion of trade, food import has increased both in terms of product range and magnitude. The Belarussian households can be exposed to OCP contained in the imported products.

Food products categorized in accordance with "Medical and Biological Requirements and Sanitary Norms of Food inputs and Products Quality" were tested [5]. The following categories were distinguished: grain and cereals, sugar and confectionary, fats, tea and spices, baby food, meat products, fish, fish products and seafood. The tests of 66 samples of grain and cereals (flour, buckwheat, rice and macaroni) imported from Poland, Hungary, USA and other countries (16 countries altogether) identified DDE in different amounts in samples. The highest concentration was registered in ice imported from Czech Republic (6 μg/kg that is 3.3 times lower than the permissible level). 17 samples (25,8%) contained γ-isomers of HCCH within the permissible level. The highest level was registered in macaroni imported from Hungary (1.0 μg/kg). The residues of DDE, α- and γ-HCCH were detected in 9 samples of sugar (imported from Ukraine) or in 45% of the tested samples. Concentration of DDE in 3 samples was close to the permissible level and in one sample reached it. 100% of samples of vegetable oil imported from Poland, Belgium, Egypt and other countries (13 countries altogether) contained the residues of DDT group (the concentration was lower that 6.0 μg/kg). All metabolites of DDT and all isomers of HCCH were detected (in amount lower that permissible) in samples of spicery. 75 samples of baby food imported from Germany, Russia, Poland and Bulgaria as well as samples of domestically produces baby food have been tested, including 40 samples of blends imported from Germany. All samples contain DDE in concentration range 1.0 – 5.0 μg/kg. No products with the concentration above the permissible level were identified. 16 out of 40 tested samples of dry milk blends contain γ-HCCH (1.0 μg/kg). 13 samples of canned meat for babies produced in Russia and Belarus and 12 samples of canned fruit for babies (Poland, Bulgaria) have been tested and all samples contain DDE (1.0-5.0 μg/kg). The highest concentration of OCP was registered in fish and fish products (95 samples from 9 countries). It should be noted that the tests frequently detected DDE and DDD and, in some cases, the whole group of DDT as well as HCCH isomers. The concentration was below than permitted but higher than in other products. For example in 3 out of 10 samples of cod liver concentration of DDT metabolites ranged between 0/29 to 0/40 mg/kg.

It can be therefore concluded that:

- all groups of imported food products including baby food contain metabolites of OCP;
- detected concentration do not exceed the permissible level; however in some samples the concentration of DDT metabolites equals the permissible level;
- fish and fish products have proved to be the most contaminated in terms of the concentration and variety of chloroorganic pesticides;
- aldrin and heptachlor have not been detected in the tested samples.

The fact of identification of residues of OCP in food products even if the concentration is insignificant is the evidence of their presence in the environment corroborating the need for monitoring. However, the estimation of health impact is more objective if the intake with foodstuff (daily consumption) is quantified for the population or for individual group of households.

The first studies intended to identify the daily intake carried out in 1974-1975 [6]. It was found out that the main dose contributors were milk, dairy products, meat and meat products and daily intake was not exceed the recommended international standards. There was not data of biological monitoring (concentration in blood or other biological substances) for that period.

The common investigation of daily intake and concentration in breast milk was made in 2000-2002 [7]. To estimate the daily intake of OCP by pregnant woman and breastfeeding women the residues of α, β and γ-isomers of HCCH, aldrin, heptachlor, DDT and its metabolites were daily diet in hospital in Minsk and Vitebsk were measured. The finding suggested that concentration of DDT and its metabolites in daily diet of pregnant and breastfeeding omen ranged 0.03 -0.07 μg/kg that is 71-167 times lower that the permissible level (0.005 mg/kg). The breast milk contamination as an indicator of the contamination of body with OCP allowing to assess the risk of breastfeeding for a child [8,9] was analyzed in different regions and towns of country (84 samples) [10]. The results suggest that all tested samples contained DDE and β-HCCH. Aldrin, heptachlor and DDD were not identified in milk. The concentration of HCCH in the samples of breast milk varies across Mozyr, Svetlogors, Soligorsk and Dokshitsy being 2-65, 2-80, 0.5-35, 2-30 μg/l respectively. The concentration of DDT+DDE in the tested samples varies within the range of 2-125, 3-50, 0.4-120, 8-58 μg/l respectively. In Mozyr, Svetlogorsk, Soligorsk and Minsk the concentration of HCCH in breast milk is 5, 15, 28.2 and 19% of samples was within the permissible level established for infant formula. 5, 20, 10.3 and 27.1% of samples in these cities were within the permissible concentration of DDT metabolites meaning that the number of samples failing to meet the norms is much higher that those meeting the standards.

The dependence of OCP discharge with milk and duration of breastfeeding is fairly complex but as a rule no considerable reduction during the surveyed period (327 days) was recorded.

Daily intake of OCP per kilogram of child's weight was estimated based on the data on concentration of OCP in breast milk and children's weight. Daily intake of HCCH exceeded the permissible levels in Mozyr and Soligirsk in 5% of cases and in 2% of cases in Minsk. Concentration of DDT metabolites (DDT + DDE) in excess of the permissible level was reported in 39% of cases in Mozyr, 32% - in Soligorsk, 48.2% - in Minsk.

So, the problem of OCP impact on human health is still acute despite the fact that their use has considerably decreased everywhere. The data on the concentration of OCP in breast milk can be taken as a criterion for estimation of the associated contamination of food products and as a basis for developing the measures to reduce the impact of pesticides on children under one year age taking into consideration that the impact of other POPs, radionuclides and nitrates reinforce the adverse impact produce by OCP.

References:

1. Report of Scientific Survey «Study of Contamination by Pesticides of Food Products in Different Regions in Country" // Belorussian Scientific Research Institute of Sanitary and Hygiene, Minsk, 1972 . - 98 P.
2. "Sanitary and Epidemiological welfare of Population in Belarus" // Annual Report (2001-2006), Republican Center of Hygiene, Epidemiology and Public Health, Minsk.
3. Concentration of organochloride pesticides residues in main food products, breast milk and adipose tissue of citizens in Belarus / E.N. Barkatina [et al..] // Storage and processing of foodsfuff. – 2002. – № 7. – P. 29-32.
4. Gas chromatography determination of residues of organochloride pesticides in main food products in Gomel Region in Belarus / E.N. Barkatina [et al.]//Mat. of anniversary conf. for 80-years of Belarussian State Medical University "Actual Questions of Medicine", Minsk, 2001. – V.1. – P. 23-26
5. Gas chromatography determination of residues of organochloride pesticides in main food products / E.N. Barkatina [et al.]// Jour. of Analyt. Chem.. – 1998. – V.53, № 9. – P. 979-983.
6. Report of Scientific Survey «Study of Contamination by Pesticides of Food Allowance" // Belorussian Scientific Research Institute of Sanitary and Hygiene, Minsk, 1975 . - 112 P.
7. Chloroorganic pesticides in main food products, Food Allowance and Breast Milk in different Regions in Belarus / E.N. Barkatina [et al.]// Mat. of Scientific Session of Belorussian Medical Academy of Postgraduate Training, Минск, 1997. – P. 21-27.
8. Quinsey, P.M. Persistence of organochlorines in breast milk of women in Victoria, Australia / P.M. Quinsey, D.C. Donohue, J.T. Ahokas/ Food and Chemical Toxicology. -1995. – Vol. 33(1). P. 49-56.

9. Somogyi A. Nurturing and breast-feeding: exposure to chemicals in breast milk / A.Somogyi, H.Beck // Environmental Health Perspectives. – 1993. – Vol. 101(SUP 2). P. 45-52.
10. Organochlorine pesticide residues in breast milk in the Republic of Belarus/ Barkatina, E.N. [et. al.] // Bulletin of Environmental Contamination and Toxicology. - 1998. - Vol. 60(2). P. 231-237.

THE ECOTOXICOLOGICAL ESTIMATION OF THE SITES POLLUTED WITH OBSOLETE PESTICIDES

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12 areas surrounding former pesticide storage warehouses were investigated. Land around the former warehouses is not fenced. Soil in these areas contains residuals of organochlorine pesticides including: 4,4'-DDT; 2,4'-DDT; 4,4'-DDE; 4,4'-DDD; α-HCH; β-HCH; γ-HCH and persistent herbicides. Concentrations of organochlorine pesticides in soil exceed maximum acceptable concentration limits for Ukraine (0.1 mg/kg) by tens to hundreds of times. To estimate a possibility of phytoremediation for cleaning up the soils polluted with pesticides, it is necessary to check their phytotoxicity first. When testing soils with long-term pesticides pollution were tested, the slow-down toxicity effect was observed. Soil phytotoxicity was studied according to the international and Ukrainian standard (ISO 11269-2:2004 Soil quality: determination of the effects of pollutants on soil flora. Part 2: Effects of chemicals on the emergence and growth of higher plants). Dernovo-podzolic soil selected near the pesticide warehouses was used for experiments. Soil for control samples was taken from virgin lands with the same soil and climatic conditions. Quantitatively-specific structure of natural flora was determined with registering frame on the diagonal of the square.

Keywords: obsolete pesticides, phytoremediation, ecotoxicological estimation.

Introduction. Starting from the 50^{th} of XX century, large number of pesticides storehouses was built on the territory of former USSR. Nowadays there are 147 large state storehouses and 4976 private storehouses in Ukraine. These storehouses keep nearly 21 thousand tons of obsolete pesticides, including about 2 thousand tons of 1,1-(bis-4-chlorophenyl)-2,2,2-trichloroethane (DDT). Many of these storehouses are ruined, some of them entirely destroyed. Due to bad storing conditions, pesticides are mixed, forming new compounds with unknown properties. Pesticides are polluting the environment by horizontal and vertical migration. An inventory of obsolete pesticides was made in Ukraine. Among them there are such persistent organic pollutants (POPs) as DDT – nearly 2 thousand tons (≈ 10% of total), Heptachlor – 13,4 t (≈ 0, 07%); Hexachlorobenzen – 1,0 t (≈ 0,005%); Endrin – 1,1 t (≈0,005%) [1]. According to the other data, pesticides Aldrin, Dieldrin, Chlordane, Mirex were not used in the Ukraine [2].

Materials and Methods. To characterize the residual amounts of pesticides in soil near pesticide warehouses we studied the soil contamination with organochlorine pesticides and their metabolites (α-, β-,γ-HCH, 4,4'-DDT, 4,4'-DDE, 4,4'-DDD, 2,4'-DDT, 2,4'-DDE, 2,4'-DDD). The identity and concentration of pesticides at the contaminated sites has not been established. Sampling was conducted according to accepted engineering specifications and state standards of Ukraine [3]. Soil samples were taken at the distance of 1, 5, 10, 15, 25, and 50 meters in four directions from a warehouse (northern, southern, western and eastern). Soil was initially stored in paper bags, then transferred to labeled plastic bags and transported to the laboratory. Soil samples were stored frozen until analysis. All soils and plants' samples were analyzed at the Institute of Agroecology according to accepted engineering specifications and state standards for Ukraine [4].

Results and discussion. As the result of DDT destruction, two other substances appear: 1,1-(bis-4-chlorophenyl)-2,2-diichloroethane (DDD) and 1,1-(bis-4-chlorophenyl)-2,2 -dichloroethene (DDE). These substances are always impurities in DDT products. Their physical and chemical properties are the same as DDT, but they are even more persistent in the environment [5].

The problem of disposal of obsolete pesticide has two aspects: utilization of substances accumulated in the storehouses, and remediation of areas polluted with toxic matters, which were formed at the places of long-time pesticide storage. Unfortunately, the problem of pesticides polluted sites remediation is not paid the required attention. The object of our investigation is soil with long-time pesticides pollution. In the Institute of Agroecology of UAAS investigations of pollution level of agricultural lands are conducted. This program also includes the study of places of local obsolete pesticides pollution and development of the methods of polluted zones remediation. Besides, soils at the places of pesticides storage are also investigated for concentration of pesticides residuals sim-triazine class derivatives: Simazine, Atrazine, Prometryn and fungicide Tilt.

Size and position of polluted sites is often different from sanity zones of pesticides storehouses. During long-time storage pesticides are connected with soil colloids making them unreachable for the microorganisms, slowing down the soil self clean-up process. Degradation of DDT in the soil can proceed in two ways, depending on the environment. In the aerobic conditions DDE is produced extremely obsolete compound. Its degradation is very slow. The product of anaerobic degradation – DDD – is less obsolete, and its decomposition is easier. To liquidate the pollution it is necessary to make classification of a soil due to level of danger of polluted sites and develop methods for their remediation. The estimation of pollution levels of polluted sites was conducted according to UN/SCEGHS/5/INF.4 in three stages [6]. *Stage 1.* Primary estimation based on the list of dangerous wastes. Soils polluted with HCH are potentially dangerous, because these pollutants are included in the list of dangerous wastes according to Appendix VIII of Basel convention. *Stage 2.* Estimation based on the concentration of toxic compounds. The main soil pollutants are HCH pesticides: 4,4'-DDT; 4,4'-DDE; and 4,4'-DDD, 2,4'-DDT, α-, β- and γ-isomers of HCH. Pesticides Hexachlorobenzen, Aldrin, Dieldrin, Endrin, Chlordane, Mirex were not located in soil samples. Now, de minimum level of HCH and DDT is 50 mg/kg for each compound. If soil is polluted with several compounds, then de minimum level is taken for their concentrations sum with corresponding coefficients (according to Basel convention, appendix VIII). If concentration of each POP all their total concentration exceeds de minimum level, then such soil is treated as a toxic waste. Soil with such a high POPs concentration has to be excavated. Plots with concentration of POPs exceeding de minimum level were located on 2 sites of 11 studied (table 1).

Maximum POPs concentration in the soil

Table 1

Storehouse position (type of soil)	Concentration, µg/kg		
	DDT	(α+β+γ)-HCH	DDT + HCH
Poltava region (chernozem)	417,51	0,69	418,20
Kyiv region (dernovo-podzolic)	2,632	182,35	184,98

For other sites total concentration of DDT and HCH does not exceed 10 mg/kg. Such soils can be remediated using ecologically safe technologies, such as phytoremediation. The area near the warehouse of mineral fertilizers and pesticides which are situated on the territory of National historical and cultural reserve «Batkivschyna Tarasa Shevchenko» (Cherkassy region) polluted with propiconazole (fungicide Tilt). The maximum concentration of propiconazole in soil is 56300 µg/kg.

We have tested *Cucurbita Pepo* plants as POPs accumulators on the typical for Ukraine dernovo-podzoilc soil. To estimate the possibility of phytotechnologies application we have conducted soil testing. *Stage 3.* Ecotoxical estimation according to the standard ISO 11269-1,2:2004. monocotyledonous (category 1) and dicotyledonous (category 2) plants were chosen for the experiments. Plants were collected after 21 days of control vegetations came up, after first signs of peripheral chlorosis – typical disease, caused by xenobiotics, which result chlorophyll destruction – appeared. Stalk length of some experimental plants was greater then the control in some cases (*Cucurbita Pepo*), but their mass was less then of the control ones. Root size was smaller then the control in all test cases compared to the control ones and varied from 15% for *Glycine max* L to 54% for *Cucurbita Pepo* (table 2).

Testing of the polluted soil

Table 2

Plant		Root length		Stalk length		Symptoms of peripheral chlorosis, day	Time of plants vegetation, days
		Cm	% of control	Cm	% of control		
Category 1							
Barley	*Hordeum vulgare* L.	7,84±1.26	80	23,28±2,35	100	28	35
Wheat	*Triticum vulgare* L.	4,69±1,44	78	25,38±2,43	83	28	35
Category 2							
Pumpkin	*Cucurbita pepo*	4,66±1,47	46	16,54±3,66	123	29	32
Squash	*Cucurbita pepo*	5,60±1,40	74	25,60±1,40	131	29	32
String bean	*Phaseolus vulgaris*	7,98±1,57	81	32,71±1,36	93	28	31
Soybean	*Glycine max* L	8,00±1,61	85	18,94±2,27	71	27	30

For the soil with long-time pesticides pollution slowed-down toxicity effect occurs, its signs appearing after the recommended ISO period (14-21 days). To approve the biotesting results, concentration of sim-triazine derivatives herbicides in the examined soil was studied. The concentration of Atrazine was 0,208; Prometrin – 0,512; Simazine – 0,135 (mg/kg). Total concentration of sim-triazine derivatives was 0,855 mg/kg in the dried soil. As agricultural crops cultivation for the aim of phytoremediation is limited because of high soil phytotoxicity possibilities, we have studied wild plants phytocenosis on the long-time DDT (0,345 mg/kg) and Prometryn (0,321 mg/kg) polluted soil around the pesticides storehouse in Kyiv region. It is appeared that quantity of plant species and density of plants covering increase with the distance from storage warehouse. (table 3).

Plants density on the polluted territory

Table 3

Direction	Species' quantity / amounts of plants at different distances from former warehouse sites for 2006 - 2007 years, units/m^2					
	0 – 1m		1 – 5m		5 – 15m	
	2006	2007	2006	2007	2006	2007
East	8 / 409	8 / 506	11 / 466	16 / 596	17 / 554	18 / 687
South	10 / 335	8 / 344	33 / 478	20 / 540	16 / 212	16 / 384
West	15 / 449	14 / 260	16 / 517	21 / 448	20 / 716	21 / 708
North	7 / 327	7 / 228	20 / 687	20 / 392	12 / 491	25 / 560
Mean value	10 / 380	9 / 335	20 / 537	19 / 494	16 / 493	20 / 585

Phytocenosis of the investigated territory (within the 50 meters radius of the warehouse) is represented by 54 species from 21 families with the domination of Asteraceae and subdomination of Poaceae. The number of botanic families increases with the distance from the source of pollution. The dominating species of the investigated territory are Achillea millefolium, Artemisia absinthium, Artemisia vulgaris, Elytrigia repens, Gallium aparine, Impafiens parviflora, Calamagrostis epigeioes, Spergula arvensis, Taraxacum officinalis, Viola arvensis, Sonchus oleraceus and Avena persica. According to preliminary results, Spergula arvensis and Taraxacum officinalis plants are capable of DDT accumulation in their tissues.

Conclusions: 1. It is necessary to monitor all areas with long-term pollution near the obsolete pesticides warehouses and to assess the levels of soil pollution. 2. Soil remediation method is chosen depending on the level of its pollution. If it's total pollutants concentration exceeds *de minimum* level (50 mg/kg for POPs), such soil is treated like a toxic waste and has to be excavated and disposed of as according to Basel and Stockholm conventions. 3. To estimate a possibility of phytoremediation application for cleaning-up the soils polluted with pesticides, it is required to check their phytotoxicity first. When testing soils with long-term pollution with pesticides were tested, the slow-down toxicity effect is observed. 4. To investigate the possibility of non-target plants for phytoremediation of polluted soils, plant families typical to the former pesticide storage sites of the Kiev region territory were studied. The pytocenosis on the studied territory is represented by 54 species of 21 families, mostly from *Asteraceae* and *Poaceae* families. The quantity of biological families increases with the distance.

References:

1. *Drozda V.* (2001) The problem of obsolete pesticides disposal in Ukraine. Solution, ecology and economy. Abstracts 6th International HCH and pesticides forum, Poznan, Poland, P.143-147.
2. The newsletter: Proof organic pollutants (POPs) in Ukraine and in the world. (2005). №11. (www. POPs_newsletter.lists.greenkit.net).
3. The unified rules of sampling of agricultural production, food stuffs and objects of an environment for definition of microquantities of pesticides. Ministry of Health of the USSR. Approved 21.08.1979.
4. Klisenko M.A., Kalinin A.A., Novikova K.F., and others. (1992). Methods of definition of microquantities of pesticides in food stuffs forages and an environment: Handbook, Vol. 1-2
5. White. J.C. 2001. Plant-facilitated mobilization and translocation of weathered 2,2-bis(p-chlorphenyl)-1,1- dichloroethylene (p,p'-DDE) from an agricultural soil. *Environ. Toxicol. Chem.* 20, 20 47-2052.
6. UNEP/CHW.6/26, 2002, 19p.

FATE OF HCHs IN THE REAL ENVIRONMENT: FIELD EXPERIMENTS IN SPOLANA CHEMICAL FACTORY

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Field studies together with laboratory simulations of various environmental processes are the key issues of modern environmental chemistry, crucially important for understanding the fate of persistent organic pollutants in the real world. Heavily contaminated site of Spolana Neratovice as former producer of organochlorine pesticides was employed in this project as the experimental field where volatilization, bioaccumulation and biotransformation processes were studied. Data derived from these experiments were used to determine the volatilization fluxes, estimate the impact of the old burdens and model the environmental distribution.

Introduction

High amounts of organochlorine pesticides were produced and applied in former Czechoslovakia in the 50´s and 60´s. 64 000 tons of DDT and 10 000 tons of toxaphene mixtures were used. On the other hand, aldrin, dieldrin, heptachlor or methoxychlor have never been produced and their usage was very limited, and chlordane and mirex have never been registered. HCB was produced in Czechoslovakia, and it was used for various agricultural and industrial applications [1].

Obsolete pesticides were partially disposed in the 60's and 70's, mainly by combustion. Liquidation of remaining stocks has been postponed until more suitable method is introduced. Since they had often been stored under inappropriate conditions and without maintaining the security precautions, they turned into significant source of environmental contamination. Proper liquidation of the old reserves has only begun after 1989 with the first part incinerated in Ingolstadt (FRG). According to documentation, this included 1 900 tons of pesticides and pesticides containing waste, out of which 50 to 60 % were persistent organic pesticides (mostly DDT and HCH). There are, however, still both, legal and illegal stocks of obsolete pesticides in the country today [1].

Both technical hexachlorocyclohexanes (HCH) and lindane (γ-HCH) were produced in Spolana Neratovice between 1958 and 1976. Total production of lindane was 3 330 tons which is about 5% from total production of technical HCH. Lindane fraction varied between less than 2% in 1958 (460 t of technical HCH, 7 t of lindane) and 10% in 1976 (2 390 t of technical HCH, 223 t of lindane). Even though HCH production was discontinued more than 30 years ago, Spolana is still significant source of environmental pollution especially during the flood events because of contaminated buildings, soils and ground water.

Current research on the global fate of POPs seeks new information on the sources of POPs [2], but also on other factors controlling air concentrations because the climate [3,4], air-surface exchange or atmospheric transport influence greatly spatial and temporal variability of atmospheric POPs concentrations [5,7]. Factors as the air-soil exchange, soil degradation and bioaccumulation were addressed in the field studies performed at heavily contaminated sites of Spolana Neratovice, Czech Republic.

Sample analysis

All air, soil and biota samples were extracted with dichloromethane in Büchi System B-811 automatic extractor. Laboratory blanks and one reference materials were analyzed at the same time. Surrogate recovery standards (PCB 30 and PCB 185) were spiked on each filter prior to extraction. PCB 121 was used as internal standard. Volume was reduced after extraction under a gentle nitrogen stream at ambient temperature, and fractionation achieved on silica gel column modified with sulfuric acid. Gel permeation chromatography was added as an extra clean-up step for biotic samples. Samples were analyzed using GC-ECD (HP 5890) supplied with a Quadrex fused silica column 5% Ph for PCBs (PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180, and OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH, p,p´-DDE, p,p´-DDD, p,p´-DDT).

Results and discussion

Volatilization fluxes of pesticides

Since volatilization of POPs from contaminated surfaces is an important source of these compounds in the atmosphere, both laboratory and field studies focused on the quantification of volatilization fluxes were performed. First experiments were done in volatilization chamber and influence of the temperature, humidity, wind velocity, soil type and vegetation cover, POPs content and concentration in the soil was studied. In follow-up field experiments, hat air sampler [8] (Fig. 1) was employed to assess the volatilization flux (N(t), ng m^{-2} h^{-1}) in the real conditions:

$$N(t) = \Delta m/\Delta t\ A, \qquad \text{(Eq. 1)}$$

where Δm (ng) is the total amount of POP evaporated from the soil and captured in the filter of the sampler, A (m^2) is the area of soil surface, N = Δm /A (ng m^{-2}) is the total volatilization loss from the square meter, Δt (h) is the time period.

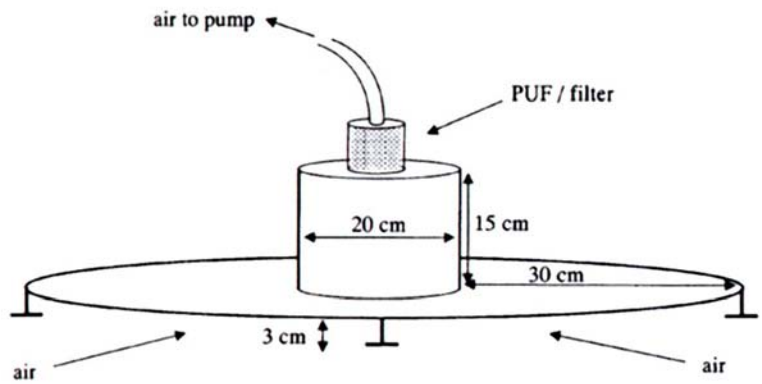

Figure 1: Scheme of the hat sampler

Based on the results of the laboratory and field volatilization studies, and on the results of detailed inventtory of contaminated soils in the Czech Republic, total volatilization flux from the soils to the atmosphere was assessed for various OCPs.

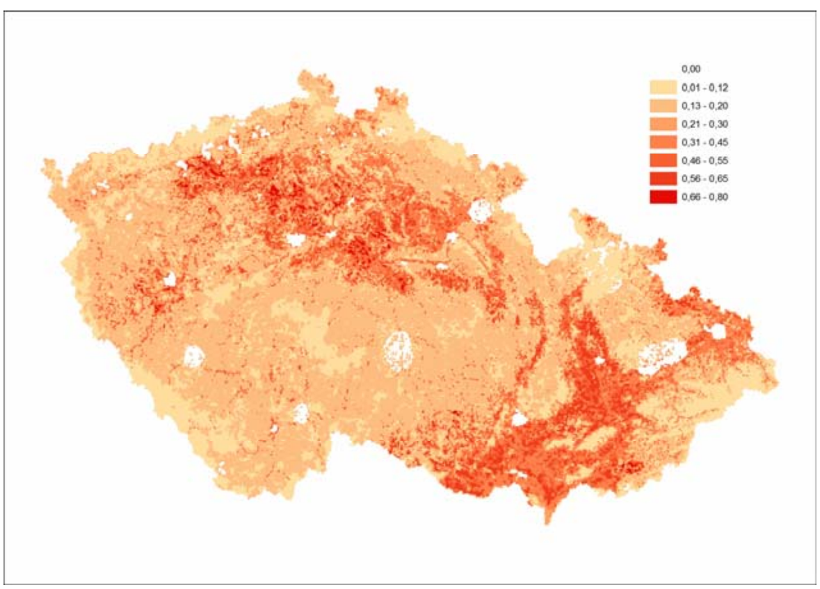

Figure 2: Volatilization flux (ng m^{-2} h^{-1}) from contaminated soils in the Czech Republic for p,p'-DDE

Fugacity fractions of pesticides

In the second case study, air and soil samples from Spolana factory were used to calculate the fugacity fractions of various pesticides and PCBs.

Fugacities of a compound in soil (f_s) and air (f_a) were calculated according to Harner et al.[9]:

$$f_s = C_sRT / 0.41\ \Phi_{OM}K_{OA} \qquad \text{(Eq. 2)}$$

$$f_a = C_aRT \qquad \text{(Eq. 3)}$$

where C is the concentration in medium (mol m^{-3}), R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K), ϕ_{OM} is the fraction of the organic matter in soil (1.7 times the organic carbon fraction) and K_{OA} is the octanol-air partitioning coefficient of the compound. The factor 0.411 improves the correlation between the soil-air partitioning coefficient and $K_{OA.}$[10-12]

The fugacity fraction (f_f) is calculated as the fugacity in soil divided by the fugacity in air and gives an indication of the net direction of air-soil exchange [9].

$$f_f = f_s / f_s + f_a \qquad \text{(Eq. 4)}$$

The fugacity fractions near 0.5 indicate equilibrium, fractions > 0.5 indicate net volatilization from the soil into air, whereas values < 0.5 indicate net deposition from air to soil. Fugacity fractions between 0.3 and 0.7 should not be considered to differ significantly from equilibrium [8,9].

Very high fractions were calculated for Spolana industrial sites. Results were further compared to other sites in the Czech Republic and countries of former Yugoslavia collected over a period of five months to assess the spatial and seasonal variability of air-soil exchange. For all OCPs there were higher median values of the fugacity fractions in the CR than in the Balkan region. α-HCH, for instance, had a median of 0.45 in the Balkan and 0.93 in the CR. Similarly, DDE and DDT median fractions were 0.32 and 0.14, respectively, in YU, but 0.62 and 0.33, respectively, in the CR. This corresponds with higher soil contamination levels in the CR: For DDE and DDT, for example, these were in the range 0.3-41.3 and 0.1-53.2 ng g^{-1} (median 1.8 and 1.3 ng g^{-1}), respectively, in the CR while they were in the range 1.0-1135.7 and 0.7-1906.9 ng g^{-1} (median 7.0 and 4.3 ng g^{-1}), respectively, in the countries of former Yugoslavia.

Descending trend of the fugacity fractions towards the colder season was observed and this seasonal trend was more pronounced for the more volatile compounds. It was, however, much less obvious at heavily contaminated sites. It can be concluded that the soil is a sink for highly chlorinated PCBs and for DDT, for DDE the status is closer to equilibrium, with a tendency to net-depositional behavior during winter and net-volatilizational during summer. For most of the PCB congeners as well as for α-HCH, the soil tends to be a source of pollution especially but not exclusively during summer. For most volatile compounds, a negative correlation of fugacity fractions with the organic carbon content in the soil was found (Fig. 3).

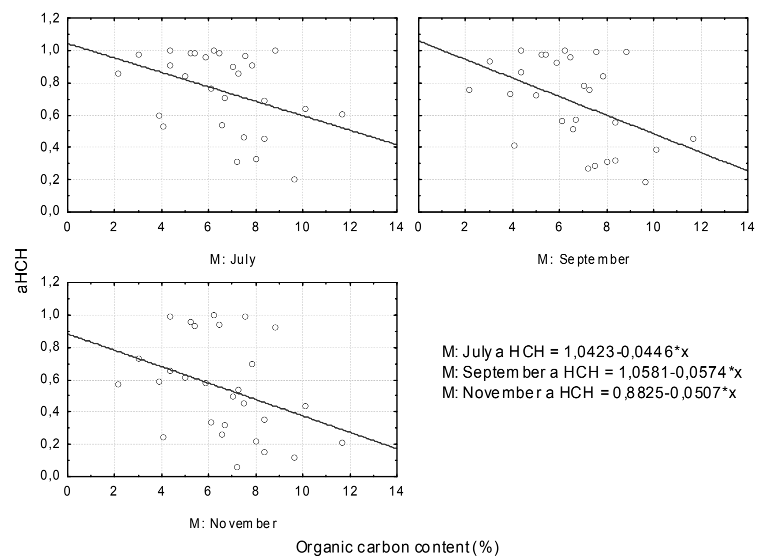

Figure 3. Correlation between the α-HCH fugacity fraction, ff, and organic carbon content in the top soil (%) - all sampling sites

Enantioselective degradation of pesticides in soils

Chiral analysis of the soil samples from industrial sites heavily contaminated with pesticides was performed to assess their enantioselective degradation in soils. Enantiomeric fractions (EF) of α-HCH, *o,p'*-DDD and , *o,p'*-DDT were determined according to equation 5:

$$EF = E+/(E+ + E-), \qquad \text{(Eq. 5)}$$

where (*E*+) is a peak area of (+) enantiomer and (*E*−) is a peak area of (-) enantiomer,

EFs varied from site to site and their value was dependent on many factors as the content of organic carbon, microbial activity of the soil, pH, and others.

Since the volatilization of pesticides from contaminated soils is an important source of these compounds in the ambient air, it can be expected that EF values of POPs in the atmosphere correspond to those in soil. Thus, EFs of selected pesticides were also calculated for the air samples taken at the same sampling sites. Irrespective of the sample origin and EF values in corresponding soils, atmospheric EF values did not differ significantly from the racemic mixture and ranged from 0.49 to 0.51 in the samples collected 1.5 m above the ground. On the contrary, when the hat sampler was used and air was sampled only few centimeters above the ground, the atmospheric EFs corresponded very well with those found in the soil. A continuous mixing of ambient air layers as well as the influence of the long-range transport of volatile compounds from other locations has to be considered when the POP source identification is attempted based on the enantiomeric fractions.

Bioaccumulation in plants

Although the bioaccumulation of persistent compounds in the crops growing at contaminated sites has been a concern, very few field studies were performed to provide real environmental data and estimate the impacts. In the last case study performed in Spolana Neratovice we focused on various ways of an uptake of POPs into the biotic tissues.

While the accumulation of the gas phase chemicals from the atmosphere is thought to be dominant transfer route, root uptake is supposed to have a minor impact. Only a few authors were, however, interested in the process of dry deposition of less volatile chemicals, which can be very important for plants with leaves or fruits in the direct contact with the soil surface.

Several plant species (lettuce, radish, corn) were employed in our case study, planted in the soils of different type and contamination level. Experimental set-up allowed us to distinguish between various routes of an uptake and accumulation of POPs in the plant tissues. Results of the field study were compared to available plant accumulation models showing that the dry deposition of chemicals on the leaf surfaces is generally underestimated route for their uptake by plants.

Conclusions

We have to conclude, that contaminated soils have to be considered as significant sources of the air pollution, some of them continuously, others seasonally. These sources should be included not only in transport and distribution models but also in the national inventories of persistent organic pollutants which are organized as part of the national implementation plans in compliance with the reporting commitments of the member states of the UNEP POPs convention.

Acknowledgements

The project was supported by the Czech Ministry of Education, Youth and Sport (MSM 0021622412), and by SPOLANA Neratovice. Authors would like to acknowledge the management of SPOLANA, as well as managements of SITA CZ and BCD CZ, companies responsible for remediation site, for the support of this project and help with the sampling campaigns.

References:

1. I. Holoubek and e. al, GF/CEH/01/003: Enabling activities to facilitate early action on the im MIKEŠ plementation of the Stockholm Convention on persistent organic pollutants (POPs) in the Czech Republic, 2003, TOCOEN REPORT No. 249.
2. W.D. Hafner and R.A. Hites, Environmental Science & Technology, 2003, 37, 3764-3773.
3. J.M. Ma, H. Hung and P. Blanchard, Environmental Science & Technology, 2004, 38, 2538-2543.
4. M.F. Simcik, I. Basu, C.W. Sweet and R.A. Hites, Environmental Science & Technology, 1999, 33, 1991-1995.
5. I.T. Cousins and K.C. Jones, Environmental Pollution, 1998, 102, 105-118.
6. T.F. Bidleman, Water Air and Soil Pollution, 1999, 115, 115-166.

7. B.R. Hillery, I. Basu, C.W. Sweet and R.A. Hites, Environmental Science & Technology, 1997, 31, 1811-1816.
8. S.N. Meijer, M. Shoeib, L.M.M. Jantunen, K.C. Jones and T. Harner, Environ. Sci. Technol., 2003, 37, 1292-1299.
9. T.Harner, T.F. Bidleman, L.M.M. Jantunen and D.Mackay, Environmental Toxicology and Chemistry, 2001, 20, 1612-1621.
10. T.F. Bidleman and A.D. Leone, Environ. Pollut., 2004, 128, 49-57.
11. M. Hippelein and M.S. McLachlan, Environ. Sci. Technol., 1998, 32, 310-316.
12. S.N. M*eijer, M. Shoeib, K.C. Jones and T. Harner, Environ. Sci. Technol., 2003, 37, 1300-1305.*

MONITORING NETWORK OF HCHs AND OTHER OCPs IN THE CZECH REPUBLIC AND CENTRAL AND EASTERN EUROPE

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The potential of passive air sampling (PAS) devices to assess the influence of local pollution sources on the quality of surrounding environment was recently investigated as well as their sensitivity to the seasonal variations in the ambient air concentrations of POPs. Following the series of experiments focused on their feasibility in the long-term measurements, and influence of various meteorological conditions on their performance, PAS were employed in several monitoring programs. Monitoring network in the Czech Republic (MONET-CZ) was established in 2004, and included industrial, agricultural, urban, rural, and background sites. It was further extended in 2006 to cover the countries of the Central and Eastern Europe (MONET-CEECs) with the general lack of information on the ambient air pollution.

Introduction

As the air pollution became an issue of great public health concern and the new regulations introduced their demands, a pressing need to obtain more POPs data in a cost-effective way appeared. Global Monitoring Network has been designed for the purpose of the Stockholm Convention with the objecttive of establishing baseline trends at global background sites [1]. When signatory parties are to conduct source inventories, identify ongoing sources, and provide environmental monitoring evidence that ambient levels of POPs are declining [2,3], developing countries in particular require cost-effective and simple approaches. Since the high volume air samplers as expensive devices requiring reliable power supply as well as trained operators are not widely available, the air monitoring of POPs has only been conducted at limited number of sites. In the last years, however, new demands resulted in development of the range of passive air samplers (PAS) as the new tools for the air quality monitoring [4-9]. PAS offer a cheap and versatile alternative to the conventional high volume air sampling as they are capable of being deployed in many locations at the same time.

It was demonstrated that passive air samplers using PUF filters are suitable to study vapor-phase air concentrations of POPs, particularly more volatile compounds [10-12], and they were successfully applied as a tool for POPs monitoring on the global [1] and regional [13] levels. Based on their unquestionable advantages, passive samplers were recommended by the Preliminary Ad-hoc Technical Working Group for the Global Monitoring Plan as a suitable tool for the global monitoring of POPs in ambient air.

Countries of the Central and Eastern Europe (CEE) are generally lacking information on the levels of persistent organic pollutants (POPs) in the environment [14]. A better situation is in the Czech Republic, Slovakia, Poland, and Slovenia; satisfactory information about the pesticides only exists in some others, like Hungary, Bulgaria and Croatia. In the rest of CEE countries, data available on POP sources and levels are very limited, and there is no systematic monitoring of POPs in the environment or humans in the countries of former Yugoslavia [15]. Considering the fact that this region has very specific environmental problems resulting from the recent wars, a need of improvement of this situation is obvious [13].

Material and Methods

Sampling technique

Passive air sampling device consists of two stainless steel bowls attached to the common axes to form a protective chamber for the polyurethane foam filter. The filter is attached to the same rod and it is sheltered against the wet and dry atmospheric deposition, wind and UV light [16]. Exposure times between four and twelve weeks enable determination of many compounds from the POP group. Average sampling rate was estimated to be 3.5 m^3/day which roughly corresponds to 100 m^3 of the air sampled during four weeks of deployment.

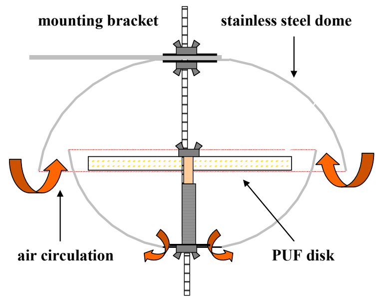

Figure 1: Scheme of the passive air sampling device

Air sampling

Passive air samplers were prewashed and solvent-rinsed with acetone prior to installation. All polyurethane filters (15 cm diameter, 1.5 cm thick, density 0.030 g cm^{-3}, type N 3038; Gumotex Breclav, Czech Republic) were prewashed, cleaned (8 hours extraction in acetone and 8 hours in dichloromethane), wrapped in two layers of aluminum foil, placed into zip-lock polyethylene bags and kept in freezer prior deployment. Exposed filters were wrapped in two layers of aluminum foil, labeled, placed into zip-lock polyethylene bags and transported in cooling box at 5°C to the laboratory where they were kept in freezer at –18°C until the analysis. Field blanks were obtained by installing and removing the PUF disks at all sampling sites.

Sample analysis

All samples were extracted with dichloromethane in Büchi System B-811 automatic extractor. One laboratory blank and one reference material were analyzed with each set of ten samples. Surrogate recovery standards (PCB 30 and PCB 185) were spiked on each filter prior to extraction. PCB 121 was used as internal standard. Volume was reduced after extraction under a gentle nitrogen stream at ambient temperature, and fractionation achieved on silica gel column; sulfuric acid modified silica gel column was used for PCB/OCP samples. Samples were analyzed using GC-MS instrument (HP 6890 - HP 5972) supplied with a J&W Scientific fused silica column DB-5MS for PCBs (PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180, and OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH, p,p´-DDE, p,p´-DDD, p,p´-DDT).

Results and Discussion

Based on the results of pilot studies,[17, 18] PAS have been first employed as a part of the regular air monitoring program in the Kosetice observatory, Czech Republic (EMEP background station) since 2003. Simultaneous employment of PAS and high volume samplers at this site provided valuable information about the performance of the passive samplers under various meteorological conditions, and demonstrated the seasonal variations (Fig. 1).

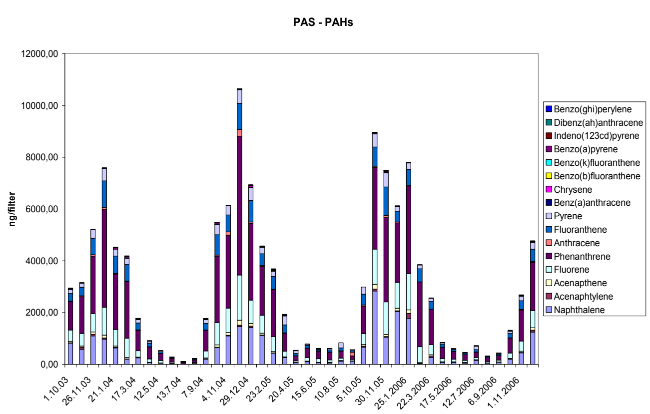

Figure 2: Seasonal variation of PAHs in the ambient air (ng/PUF filter), Kosetice observatory, Czech Republic

Starting 2004, a long-term PAS monitoring of the various local sources (petrochemical and chemical enterprises, industrial, urban, rural and background sites) in the Czech Republic was established. PAS network was completed with a number of mountain sites estimating the role of the long-distance transport in 2006.

Apart from Spolana sites (Fig. 3), HCH congeners were almost uniformly distributed in the area of the Czech Republic (Fig.4) ranging between units and tens of ng per filter (tens to hundreds of pg m^{-3}). There was not much difference between the industrial, urban, and rural sites; surprisingly some mountain backgrounds seemed to have levels slightly higher than others. Seasonal fluctuations were more obvious on highly contaminated sites again; maxima were achieved in the warm season. Soil samples had the same distribution. While there was a very high concentration of HCHs in Spolana (up to 5 μg g^{-1}), all the other concentrations were much lower (between 100 pg and 10 ng g^{-1}). In case of soils, mountain backgrounds were about one order of magnitude lower in HCH concentrations than industrial and urban sites.

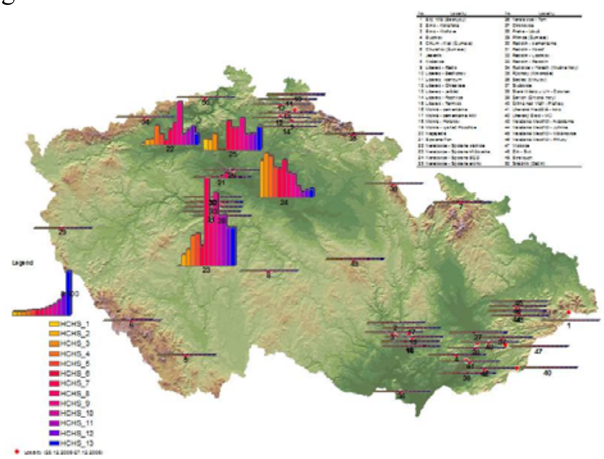

Figure 3: HCH levels (sum of α, β, γ, δ-HCH) in the ambient air (PAS, ng $filter^{-1}$) in the Czech Republic, 2006

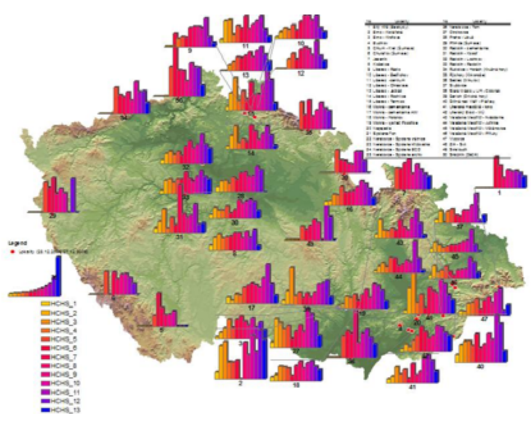

Figure 4: HCH levels (sum of α, β, γ, δ-HCH) in the ambient air (PAS, ng $filter^{-1}$) in the Czech Republic (hotspots omitted), 2006

Building on promising results of the Czech monitoring network, first steps were taken towards extending this project to cover most of the Central and Eastern Europe. Sampling sites in Estonia, Lithuania, Latvia, Romania, Slovakia, Serbia, Bosnia and Herzegovina have been monitored since 2006, with more countries joining the project in 2007.

HCH atmospheric levels in Baltic countries were similar to the ones found in the Czech Republic excluding the Spolana hotspot. Levels in Slovakia are some 50% higher than CR and similar to Bosnia, in Serbia they are four times higher that CR. Highest air contamination was found in Romania. Atmospheric maxima of 2.8 μg filter^{-1} were comparable to the Czech Republic but the median value was one order of magnitude higher that CR because elevated levels of atmospheric HCHs were found at many sites.

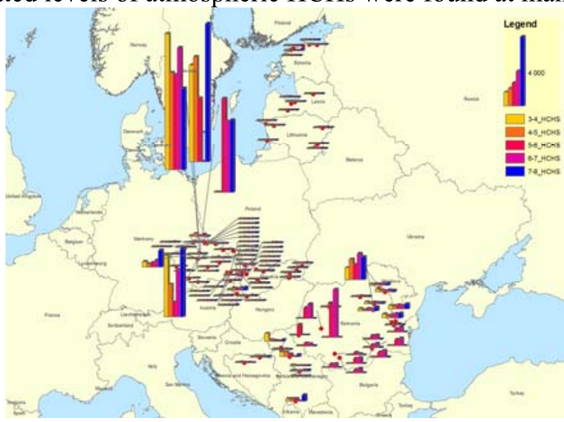

Figure 5: HCH levels (sum of α, β, γ, δ-HCH) in the ambient air (PAS, ng filter^{-1}) in Central, Eastern and Southern Europe, March - August, 2006

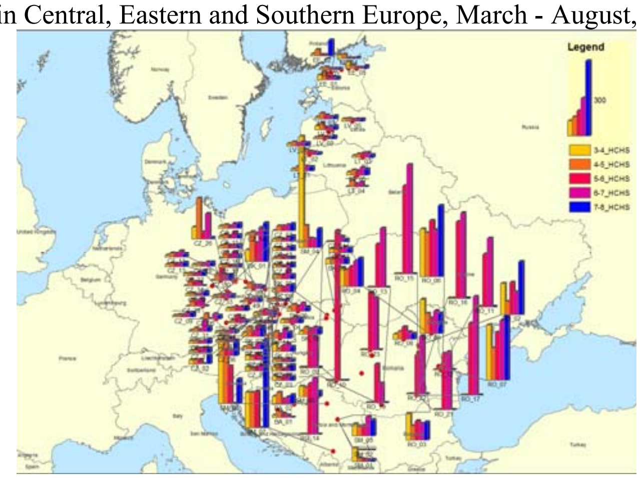

Figure 6: HCH levels (sum of α, β, γ, δ-HCH) in the ambient air (PAS, ng filter^{-1}) in Central, Eastern and Southern Europe (hotspots omitted), March - August, 2006

Conclusions

We can conclude that passive sampling technique is fully applicable in the long term monitoring projects and capable to fulfill the tasks of determination of levels of POPs in the ambient air, evaluation of the spatial and temporal trends in distribution of POPs, impact evaluation of point and diffusive sources, and assessment of the short- and long-range transport of POPs. All of these are important in the process of establishment a relevant arrangements for effectiveness evaluation of the international conventions and fulfilling the international obligations of the Czech Republic.

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References:

1. T. Harner, K. Pozo, T. Gouin, A.M. Macdonald, H.Hung, J.Cainey and A.Peters, Environmental Pollution, 2006, 144, 445-452.

2. UNEP, Stockholm Convention on Persistent Organic Pollutants, 2001.
3. T. Harner, M. Bartkow, I. Holoubek, J. Klanova, F. Wania, R. Gioia, C. Moeckel, A.J. Sweetman and K.C. Jones, Environmental Pollution, 2006, 144, 361-364.
4. A.J. Peters, D.A. Lane, L.A. Gundel, G.L. Northcott and K.C. Jones, Environmental Science & Technology, 2000, 34, 5001-5006.
5. T. Harner, N.J. Farrar, M. Shoeib, K.C. Jones and F. Gobas, Environmental Science & Technology, 2003, 37, 2486-2493.
6. U.M. Shahir, Y.H. Li and T.M. Holsen, Aerosol Science and Technology, 1999, 31, 446-455.
7. P. Tremolada, V. Burnett, D. Calamari and K.C. Jones, Chemosphere, 1996, 32, 2189-2203.
8. L. Wennrich, P. Popp and C. Hafner, Journal of Environmental Monitoring, 2002, 4, 371-376.
9. M.E. Bartkow, D.W. Hawker, K.E. Kennedy and J.F. Muller, Environmental Science & Technology, 2004, 38, 2701-2706.
10. F.M. Jaward, N.J. Farrar, T. Harner, A.J. Sweetman and K.C. Jones, Environmental Toxicology and Chemistry, 2004, 23, 1355-1364.
11. F.M. Jaward, N.J. Farrar, T. Harner, A.J. Sweetman and K.C. Jones, Environmental Science & Technology, 2004, 38, 34-41.
12. T. Harner, M. Shoeib, M. Diamond, G. Stern and B. Rosenberg, Environmental Science & Technology, 2004, 38, 4474-4483.
13. J.Klanova, J.Kohoutek, P.Cupr and I.Holoubek, Environment International, 2007, doi:10.1016/ j.envint. 2007.02.004.
14. UNEP, Regionally Based Assessment of Persistent Toxic Substances. Europe Regional Report., 2002.
15. UNEP, Regionally Based Assessment of Persistent Toxic Substances. Mediterranean Regional Report., 2002.
16. M. Shoeib and T. Harner, Environmental Science & Technology, 2002, 36, 4142-4151.
17. J.Klanova, J. Kohoutek, L. Hamplova, P. Urbanova and I. Holoubek, Environmental Pollution, 2006, 144, 393-405.
18. P.Cupr, J.Klanova, T.Bartos, Z.Flegrova, J.Kohoutek and I.Holoubek, Environmental Pollution, 2006, 144, 406-413.

CHEMICAL ASSESSMENT OF THE BAHLUI RIVER, IN NORTH-EASTERN ROMANIA. CASE STUDY: PESTICIDES AND PERSISTENT ORGANIC POLLUTANTS (POPS)

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The scope of the present study was the investigation of the widespread use of POPs and pesticides in the basin of Bahlui River, which is the main and the most polluted tributary of Pruth River (in north-eastern Romania).

Research is needed to assess the environmental impact of a wide range of these substances in environment, to develop currently available approaches as well as new methodologies, which allow sustainable, environmental-friendly development.

The investigation comprises the determination of non-ortho PCBs, mono-ortho PCBs and di-ortho PCBs, concentration of HCHs, DDT and their metabolites and PAHs.

In order to meet the European and worldwide requirements for fresh water protection, we propose a qualitative and quantitative assessment of water pollution with these compounds.

The results indicated that the concentration of PCBs, OCPs and PAH reported herein were markedly lower than those reported for the sediments collected 1998 from the Bahlui river by Institute of Inland Water Management and Waste Water Treatment RIZA, The Netherlands (2000) or those reported by Dragan et al (2006), while the OCP levels founded in this study are similar to that reported by Dragan et al (2006).

Key-words: PCB, DDT, PAH, chemical assessment.

Introduction

Sustainable development has an important global dimension. Many of the challenges to sustainability require global action to solve them. The overall aim is to take urgent action to secure a better quality of life for present and future generations along with a sustained economic growth, which supports social progress and respects the environment, a social policy, which underpin economic performance, and a cost-effective environmental policy.

Control of pollutants has high priority and has resulted in a number of directives to reduce emissions. Limited information is available on the fate, behaviour and effects of other major classes of POP´s and very little data are available on concentration in the environment.

Moreover, in order to meet the European and worldwide requirements for fresh water protection, we propose a qualitative and quantitative assessment of water pollution with Pesticides and Persistent Organic Pollutants (POPs). The objective of the present study was the investigation of the widespread use of POPs and pesticides in the basin of Bahlui River, which is the main and the most polluted tributary of Pruth River (in north-eastern Romania).

Experimental

Sediment samples (n=28) were collected monthly from February to November 2006 by manual coring (0-25 cm) from the River Bahlui in Iasi, Romania. The samples were dried at room temperature. Experimental conditions have been previously described in detail (El-Kady et al, 2007).

Results and Discussion

The investigation comprises the determination of non-ortho PCBs, mono-ortho PCBs and di-ortho PCBs. The results (Figure 1) showed that indicator PCBs concentrations (28, 52, 101, 138, 153 and 180) were higher than non-ortho and mono-ortho PCB concentrations constituting 70 to 80% of the total amount of PCBs. These six PCBs are environmentally very persistent and predominantly present in most PCB mixtures and in environmental samples (Aune et al., 1999). These six PCB (congeners) known as indicator or marker PCBs, account for ca. 50% of the commercial mixtures of PCB. It is difficult to correlate the congener profile with the source.

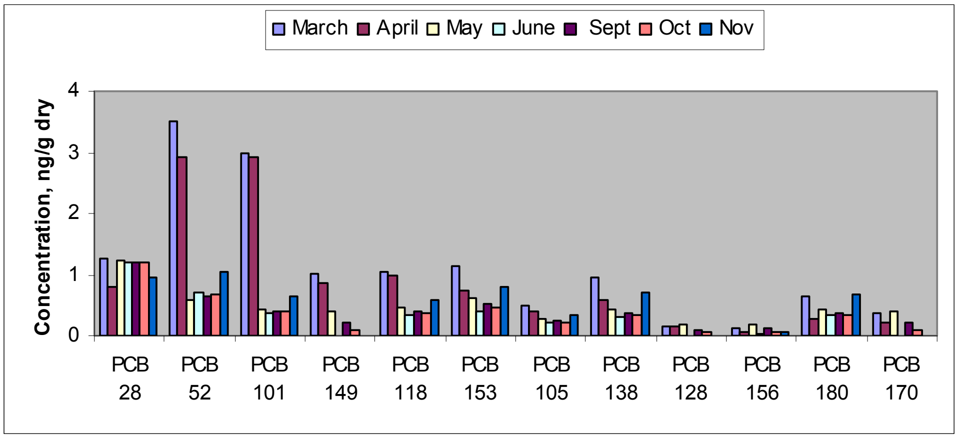

Figure 1. PCBs analysis of sediment samples from Bahlui River, Site 2.

In all samples, penta- and hexa- CBs were predominant, followed by tri-, tetra and hepta-CBs. In general, PCB concentrations in Bahlui sediments were relatively low in this study. The low levels of PCBs correspond with the lack or low production and usage of PCBs in Eastern European countries (Brevik et al., 2002).

Concentration of HCHs ranged for both sites from 0,4 to 3 ng/g dw with a higher contribution of the γ-HCH (30-70%), followed by β HCH (20-50%). The β-HCH isomer was found at lower concentrations or even not detected outer city sites.

DDTs were found at higher concentrations than HCHs and ranged from 0,56 to 18 ng/g dw and 0,18 to 4 ng/g dw for Site 1 and Site 2, respectively (Figure 2). The parent compound, pp-DDT, could be detected only in low concentrations (up to 5ng/g dw) and contributed with less than 30% to the sum of DDTs in sediment. The principal contributors of the ∑DDTs in sediment were pp-DDE, pp-DDD. The op-DDD and –DDT isomers were minor contributors to the sum of DDT. The data are consistent with previous findings for other rivers (Danube tributaries, Volga).

Combustion of fossil fuels, waste incineration, and oil spills are the potential sources of PAHs in the environment (e.g., Law, 1994; Savinov et al., 2000; Kannan et al., 2005). Because of their hydrophobicity, also PAHs show high persistence in marine sediments. PAHs were found at higher concentrations than DDTs and ranged from 36 to 155 ng/g dw and 6 to 36 ng/g dw for Site 1 and Site 2, respectively. Fluoranthene was predominant (up to 40%), followed by phenantrene (up to 30%), naphthalene (up to 35%) and benzo (g,h,i) perylene (up to 23%). The possible source of PAHs in sediments may be assessed by the ratios of individual PAH compounds (Benhlahcen et al., 1997; Klamer and Fomsgaard, 1993). A ratio of phenantrene/antracene < 10 and fluoranthene/pyrene > 1 tends to indicate that PAH contamination is from combustion processes (Benhlahcen et al., 1997). Our results met the above criteria. The results seem to suggest that PAHs in the area are derived from the combustion of fossil fuels.

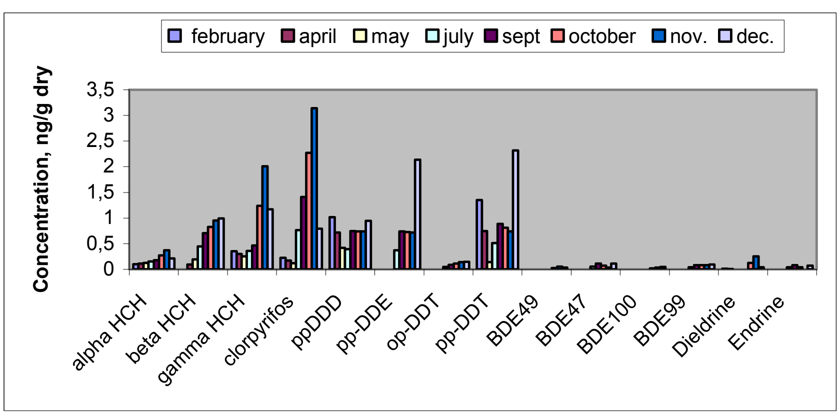

Figure 2. Chemical assessment of sediment samples from Bahlui River, Site 1.

Conclusion

The current results clearly indicated that the concentration of PCBs, OCPs and PAH reported herein were markedly lower than those reported for the sediments collected 1998 from the Bahlui river by Institute of Inland Water Management and Waste Water Treatment RIZA, The Netherlands (2000) or those reported by Dragan et al (2006), while the OCP levels founded in this study are similar to that reported by Dragan et al (2006).

Acknowledgements

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References:

1. Aune M, Atuma S, Darnerud P, Wicklund-Glynn A, Canttingius S (1999): Organohalogen Compd. 44, 93.
2. Benhlahcen KT, Chaoui A, Budzinski H, Garrigues Ph (1997): Marine Pollution Bulletin 34, 298-305.
3. Breivik K, Sweetman J, Pacyna JM, Jones KC (2002): The Science of the Total Environment 290, 181-198.
4. Dragan D, Cucu-Man S, Dirtu AC, Mocanu R, Van Vaeck L, Covaci A (2006): Intern. J. Environ. Anal. Chem. 86(11), 833-842.
5. El-Kady AA, Abdel-Wahnhab MA, Henkelmann B, Belal MH, Morsi MK, Galal Sm, Schramm KW (2007): Chemosphere 68, 1660-1668.
6. Kannan K, Johnson B-R, Yohn SS, Giesy JP, Long DT (2005): Environ. Sci. Technol. 39, 4700-4706.
7. Klamer HJC, Fomsgaard L (1993): Marine Pollution Bulletin 26, 201-206.
8. Law RJ (1994): Mar. Pollut. Bull. 29, 235-241.
9. Savinov VM, Savinova TN, Carroll J, Matishoy GG, Dahle S, Naes K (2000): Mar. Pollut. Bull. 40, 807-818.
10. Analyses of water and sediments quality of water system in the Prut basin, Romania. Report of the Institute of Inland Water Management and Waste Water Treatment RIZA, The Netherlands. 2000.

ENVIRONMENTAL POLLUTION AND AUTOIMMUNE DISEASES

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Nowadays autoimmune diseases belong to major medical problems. Scientific data demonstrating that chemicals, including pesticides, are capable to cause autoimmune diseases in humans is scarce.

Our aim was to study the relationship "pesticides and immune toxicity" with the focus on autoimmune diseases of thyroid gland as the most widespread autoimmune pathology state in Armenia.

Antibodies to thyroglobulin (TG) and thyroid peroxidase (TPO) were selected as markers of autoimmune course of thyroid gland diseases and blood serum TSH, $T_{3,}$ T_{4}- free levels determined.

Cohorts under study involved inhabitants from

1. rural regions of high application of agrochemicals;

2. mountainous regions of low application of chemicals.

In both Cohorts, there were elevated levels of antibodies to TG and TPO in all cases of autoimmune thyroiditis, bringing forth hypothyreosis.

In Cohort 1, we revealed that in 46% of patients with hyperthyroiditis, TG and TPO levels were elevated, while in Cohort 2 only in 22% of all cases of hyperthyreosis the course of a disease was an autoimmune one. Thus, as the cause of autoimmune course of this disease we can suggest the interaction of environmental chemicals (pesticides).

To our mind, high risk for development of mentioned autoimmune pathology in thyroid gland is conditioned by the chemical factor.

Reducing exposures to potentially immunotoxic compounds is important, especially in farming areas where people are directly exposed to pesticides.

Key words: autoimmune diseases, chemicals, pesticides, pollution, thyroid gland.

Nowadays autoimmune diseases belong to major medical problems. High levels of morbidity related to autoimmune pathology are registered in regions of developed industry and environmental pollution. In the US, about 6.5 million people are affected with the most widespread autoimmune disease - rheumatoid arthritis. Despite convincing results in animals, there is practically no literature data demonstrating that chemicals, including pesticides, are capable to cause autoimmune diseases in humans.

The study was aimed to reveal the relationship "pesticides - immune toxicity". Our attention was focused on autoimmune diseases of thyroid gland as the most widespread autoimmune pathology state in Armenia. Our main task was to study autoimmune diseases prevalence in regions of intense chemization. Auto-antibodies to thyroglobulin (TG) and thyroid peroxidase (TPO) were used as markers of thyroid gland diseases caused by autoimmune processes. We selected antibodies to thyroglobulin (TG) and thyroid peroxidase (TPO) as markers of autoimmune course of thyroid gland diseases. In order to differentiate hyperthyreosis and hypothyreosis we determined blood serum TSH, $T_{3,}$ T_{4}- free levels.

Cohorts under study involved:

1. inhabitants from rural regions of high application of chemicals;
2. inhabitants from mountainous regions where application of chemicals is low or absent.

In a studied Cohort 1, the intense and frequently uncontrolled pesticide application, which is a result of certain difficulties encountered in a period of economy in transition, caused not only toxic, allergic, mutagenic and carcinogenic effects, - cases of breast, gastro-intestinal, and thyroid cancer are registered. For the first time we traced the influence of pesticides to the immune system, which brought forth autoimmune diseases.

In both Cohorts, there were elevated levels of antibodies to TG and TPO in all cases of autoimmune thyroiditis, bringing forth hypothyreosis. In Cohort 1, we revealed that in 46 % of patients with hyperthyroiditis, TG and TPO levels were elevated, while in Cohort 2 only in 22% of all cases of hyperthyreosis the course of disease was an autoimmune one. Thus, as the cause of autoimmune course of primary hyperthyreosis we can suggest the interaction of environmental chemicals (pesticides).

Our observation demonstrated that the most widespread autoimmune diseases were associated with thyroid gland dysfunction. Elevated levels of TG and TPO antibodies were observed in 70% of patients with autoimmune thyroiditis, primary hyperthyroidism, and thyroid cancer.

High levels of morbidity due to different autoimmune pathology were noted in regions of developed industry and high levels of environmental pollution by chemicals (pesticides, fertilizers, etc.).

Thus, to our mind, high risk for development of such immune pathology of thyroid gland as hyperthyreosis is conditioned by chemical factor. Reducing exposures to potentially immunotoxic compounds is important, especially in farming areas where people are directly exposed to pesticides. Triggering mechanisms and exact pathogenesis of autoimmune diseases is still unknown and remain to be revealed. Certain immunological, genetic, viral, drug-induced, and hormonal factors, isolated or joint, are considered. The significant role of environmental chemicals was demonstrated in our study. Unfavourable environmental factors are supposed to cause organ-specific autoimmune diseases (e.g. thyroid diseases).

References:

1. Dumanyan D., Nersesyan S. A., Avagyan H. Thyroid Status in Population of Armenia under the Conditions of Relative Iodine Deficiency. In: Abstract Book of the First Milan Thyroid Cancer Conference. Milan, Italy, July 1-2, 2004. P. 50.
2. Environmental Pesticide Pollution and Cancer: Revealing Probable Links by the use of Tumor Markers. Toxicology and Applied Pharmacology, Volume 197, No.3, June 15, 2004, p. 337-338. P. Abstract No.795 (ICT X – 2004).
3. Noel R.Rose and Joseph B. Margolick. The Immunological Assessment of Immunotoxic Effects in Man. In: David S. Newcombe, Noel R.Rose and John C. Bloom, eds. Clinical Immunotoxicology. (Raven Press, New York: 1992), 9-25.
4. Repetto R. and Sanjay S. Baliga. Pesticides and the Immune System: the Public health Risks. World Resources Institute. Executive Summary. March 1996.
5. Screening Investigation of Thyroid Status in Population of the Republic of Armenia under Conditions of Relative Iodine Deficiency. Medical Science in Armenia, 2004, No 3.
6. World Health Organization, International Workshop: Setting Priorities in Environmental Epidemiology. Archives of Environmental Health. July/August 1994, 49 (4): 239-245.

SURFACE WATER CONTAMINATION BY ORGANOCLORINE PESTICIDES RESIDUES IN UZBEKISTAN

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Organochlorine pesticides as DDT and HCH (POPs) have been prohibited in Uzbekistan. These pesticides can be preserved in soil for long time and enter from agricultural fields to surface water with drainage, wash-out and snowmelt water. Therefore, monitoring of these pesticides in surface water remains very actual. In this paper the results of pesticides monitoring in surface water in Uzbekistan in 2000-2004 have been analyzed. They show tendency to decrease in surface water contamination by pesticides in Uzbekistan. For the period of observations, small concentrations of HCH isomers were determined in surface water, DDT and its metabolites DDD and DDE were not determined in surface water samples.

Key words: Organochlorine pesticides, residue, surface water, contamination, assessment.

Introduction

The wide use of pesticides results to their distribution as most hazardous contaminants in the environment. Under the influence of various factors pesticides are transformed and migrate from soil to other components of the environment. The research results show that 20-65% of pesticides used in agriculture remain in the places of their application: 30-50% remains in air, 4-20% – in plants, 1-10% are absorbed by surface layer of the soil, 1-5% enter the surface water and 5% migrate to bottom layer of the soil and groundwater [1].

In Uzbekistan environmental and surface water contamination by pesticides was very actual problem in 1960-1990 because of its large use for increasing cotton yield. Although the pesticides use have decreased in Uzbekistan for last 15-10 years, the problem of environmental contamination by pesticides continue to be actual because at present new pesticides are used in agriculture. Uzbekistan State Register of Chemical and biological plant protection reagents involves more than 180 substances (i.e. pesticides and others) allowed for using in agriculture [2].

Pesticides enter surface water by various ways. The organochlorine pesticides (COPs), especially HCH and DDT are very hazardous for water ecosystems and fish. These pesticides are persistent in the environment and can be accumulated in food chain until hazardous levels even if their amounts in water and bottom sediments are very small.

Despite the fact that, the use of DDT have been prohibited since 1983 and HCH since 1994 in Uzbekistan, control of these pesticides in surface water continue to be very actual. In this paper the results of pesticides monitoring in surface water in Uzbekistan in 2000-2004 have been analyzed [3].

Sampling

Monitoring points of Uzhydromet (Centre for Hydrometeorological Service of Uzbekistan) are located in rivers, small watersheds, irrigation canals, collectors and water reservoirs. Observation time in these points is set taking into account the hydrological regime of each watershed. In small rivers in mountain and sub-mountain areas and in water reservoirs, the observation frequency is from 3 up to 12 times per year. In rivers, irrigation canals and collectors water sampling is carrying out monthly [4].

Methods

Organochlorine pesticides analysis is carried out by gas chromatography method with electron capture detector [5].

Maximum allowable concentration (MAC) of pesticides in watersheds for sanitary-household water use have been used for assessment of water contamination, this value for HCH isomers is 0,02 mg/dm^3 and for DDT and its metabolites is 0,1 mg/dm^3 [6]. For water of fishery watersheds the MAC of HCH isomers, DDT and metabolites should be equal to zero [7].

Results and discussion

Water quality network of Uzhydromet carries out analysis of COPs in more than 95 monitoring points (approximately 900 water samples per year) (Fig. 1). According to monitoring data HCH isomers were detected in water samples frequently, but during observation time DDT and its metabolites were not detected in water samples.

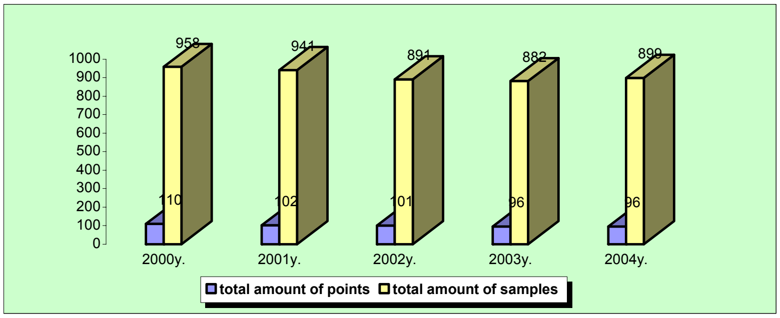

Figure 1. Total amount of monitoring points and water samples, analyzed for pesticides in 2000-2004

Maximal concentrations of HCH isomers did not exceed 0,2 ug/dm^3. Annual mean concentration for α-HCH was 0.007-0.015 ug/dm^3 and for γ-HCH was 0.004-0.16 ug/dm^3 (Tabl.1).

Pesticides residues in watersheds of Uzbekistan

Tabel 1

Year	Concentration, ug/dm^3			
	range		mean	
	α-HCH	γ-HCH	α-HCH	γ-HCH
2000	0-0,040	0-0,013	0,007	0,004
2001	0-0,022	0-0,018	0,007	0,004
2002	0-0,056	0-0,084	0,008	0,007
2003	0-0,090	0-0,071	0,015	0,011
2004	0-0,074	0-0,195	0,011	0,016

Distribution of water samples within HCH-isomers' concentration intervals are shown in Table 2. Detected concentrations of pesticides do not exceed the national MAC for sanitary and household water use.

Distribution of water samples within HCH-isomers concentration intervals

Table 2

Interval of concentration, ug/dm^3	Pesticide			
	α-HCH		γ-HCH	
	Number of samples	%	Number of samples	%
< 0.010	671	77.13	382	82.86
0.010-0.049	190	21.84	74	16.05
0.050-0.100	9	1.03	3	0.65
> 0.100			2	0.44
	870	100.00	461	100.00

According to monitoring data, detection frequency of COPs in water samples was 21.2% for α-HCH and 8.6% for γ-HCH in 2000, and 10.2% for α-HCH and 4.9% for γ-HCH in 2004 (Fig.2).

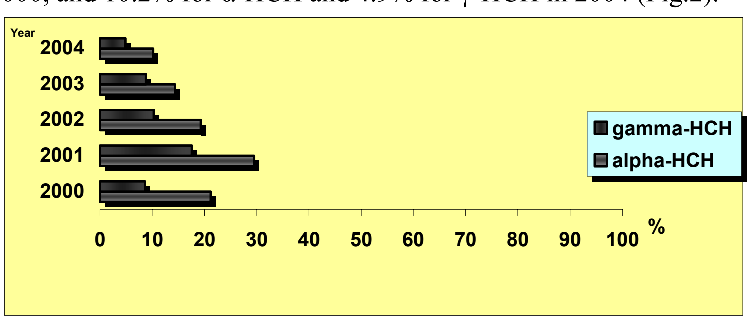

Figure 2. Detection frequency of pesticides in water samples

Percentage of monitoring points with detected pesticides amounted to 60.9% for α-HCH and 30.0% for γ-HCH in 2000, and 40.6% for α-HCH and 25.0% for γ-HCH in 2004 (Fig.3).

The most contaminated samples were from collectors and rivers in areas with intensive agricultural practices. It was determined that small watersheds and rivers in mountain and sub-mountain regions are not contaminated by pesticides.

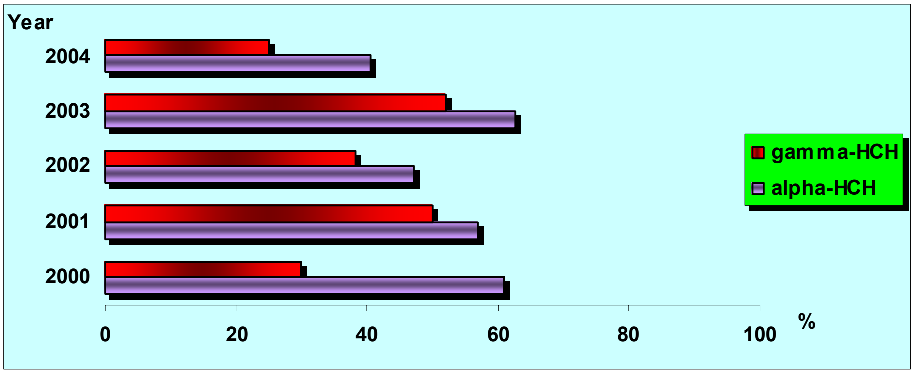

Figure 3. Percentage of monitoring points with detected pesticides

Conclusions

Surface water quality monitoring data in 2000-2004 shows the decrease in detection frequency and contamination of most watersheds and water reservoirs by pesticides in Uzbekistan. Insignificant concentrations of HCH isomers have been detected in water samples. DDT and its metabolites were not detected in surface water samples in 2000-2004.

The results of research allow concluding, that the surface water contamination by organoclorine pesticides is decreasing in Uzbekistan due to prohibition of HCH and DDT use and decreasing of other pesticides use in agriculture.

References:

1. Waddel T.E., Bower B.T. Soil Water Conserv. 1988. V. 43. No.3. P.241.
2. Register of Chemical and Biological Plant Protection Reagents, allowed to use in Uzbekistan. Tashkent. 2003. 200 p.
3. Surface water quality year-book in the activity territory of Glavgidromet for 2000-2004. Tashkent. Glavgidromet.
4. RH 68-02:2000. Management directive. Manual on sampling of water and bottom sediments in the surface water quality monitoring stations in Aral Sea basin. Tashkent. Glavgidromet. SANIGMI. 2000. 61 p.
5. RD 52.24.66-88. Manual on organohalogen pesticides and their metabolites determination in surface water. Rostov-in-Don. 1988. 40 p.
6. Bespamyatnov G.P, Krotov Yu.A. MAC of chemical substances in the environment. Moscow. Chemistry. 1985. 528 p.
7. List of maximal allowable concentrations and tentatively safe levels of impact of hazardous substances for water of fishery watersheds. Moscow. Kolos. 1993. 140 p.

CHEMICAL REDUCTION OF HCH IN GROUNDWATER

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The Netherlands

The effectiveness of treatment of HCH contaminated groundwater by chemical reduction with Zero Valent Iron (ZVI) was investigated in a laboratory study. Results were compared with the effectiveness of anaerobic biodegradation of HCH. Of three different types of ZVI tested to determine the effectiveness of chemical reduction of the HCH isomers in groundwater (granular ZVI, fine ZVI, and nanoscale ZVI) granular and fine ZVI were most effective. The batch tests have shown that ZVI can bring about a fast reduction of HCH to almost exclusively benzene. Using the aqueous phase data from the batch tests, an average half-life of 0.46 day can be estimated for total HCH. Furthermore considerable adsorption of HCH on iron was observed. Granular ZVI was selected for testing in column experiments. After 110 days and 62 pore volumes of flushing, the HCH level was still below the detection limit (0,01 µg/L) and benzene was present in a concentration of 2 µg/L, accounting for only 7.5% of the HCH in the influent. Adsorption to the solid phase will have influenced the effluent levels of HCH and degradation products in both the biological and the chemical experiments. The anaerobic biodegradation experiments demonstrated treatment efficiencies of more than 95% at retention times of 2,5 days.

Key words: Biodegradation, chemical reduction, Zero valent iron (ZVI), Permeable reactive barrier (PRB), groundwater treatment, HCH, in situ.

Introduction

After removal of waste on HCH production and storage sites contaminants will remain in soil and groundwater. On production sites considerable contamination may have entered the soil as reaction products containing liquids (brine) were often stored on the soil surface. Although solubility of HCH in groundwater is low, dissolved HCH will tend to migrate into the subsurface, and will distribute along groundwater flow paths. As HCH is mostly a persistent compound in soil receptors may become affected by the groundwater contamination. A complete remediation of soil and groundwater on the site is often not feasible on short term, but a risk assessment may identify the need of containment of the contamination in the subsurface.

A characteristic feature of the storage sites is that they are typically located in agricultural areas without infrastructure and educated personnel required for the operation of remedial action. Therefore there is a need for extensive technologies that can be applied with a limited operational effort. Reactive barriers were developed for containment of groundwater contamination migrating from source areas, with a minimum of maintenance effort. In reactive barriers contaminated groundwater is captured and treated in a subsurface passive chemical or biological treatment zone. Soil properties are amended to obtain an environment favorable for contaminant treatment. There is considerable experience with the in situ treatment of chlorinated solvents by subsurface reactive barriers based on anaerobic degradation or chemical reduction by zero valent iron [ITRC, 2005; RUBIN]. This paper focuses on the applicability of reactive barriers for containment of HCH contamination in groundwater.

At the site under study HCH was produced. The waste of the lindane production was stored on site and infiltrating rainwater caused a groundwater contamination. The groundwater contamination migrates off site and needs to be captured and treated. For the selection of a system for groundwater treatment the effectiveness of two processes were investigated in a laboratory study:

- anaerobic biodegradation;
- chemical reduction by Zero Valent Iron (ZVI).

Both processes can be utilized in situ in reactive barriers or in an on site treatment plant. The anaerobic treatment of HCH is a well known process [Langenhoff, 2002], but the effectivity of treatment of HCH with ZVI is unknown.

Degradation of HCH

From laboratory and field studies it is known that the beta- and delta-isomers of HCH can not be biodegraded by aerobic soil bacteria. All isomers are degradable in an anaerobic environment but the degradation process is slow. Reaction products of the anaerobic biodegradation are benzene and monochlorobenzene (MCB).

These products are often observed in anaerobic aquifers contaminated with HCH. Benzene and MCB are relatively stable in an anaerobic environment, but are readily degradable in an aerobic environment.

In the last years it has been observed that reduced iron minerals have the ability to transform a wide range of oxidized halogenated compounds. Zero valent iron has been identified as having the potential for abiotic transformation of chlorinated solvents in groundwater. The primary reaction mechanism postulated for this abiotic degradation of chlorinated solvents is the β-elimination pathway. As with biological reduction, the most oxidized chlorinated solvents show the highest degradation rates. Based on the composition and the feasibility of biological anaerobic degradation the chemical reduction may also be an applicable process for HCH treatment.

It is expected that the chemical reduction will also lead to monochlorobenzene (MCB) and benzene. An aerobic environment is needed to degrade these degradation products. Many aquifers are aerobic by nature and posses biological properties to attenuate the degradation products.

Experimental

The setup of the experiments is given in table 1. The process of chemical reduction will be investigated in batchexperiments, before a column experiment is set up.

Setup of the experiments

Table 1

	Batch test	**Column test**
Anaerobic degradation	-	+
Zero valent iron	+	+

Anaerobic degradation

Two stainless steel columns have been constructed with a length of 1 m and an internal diameter of 0.11 m, resulting in a volume of 9.5 L. Sampling points were installed at intervals of 25 cm. Figure 1 presents a schematic overview of the setup.

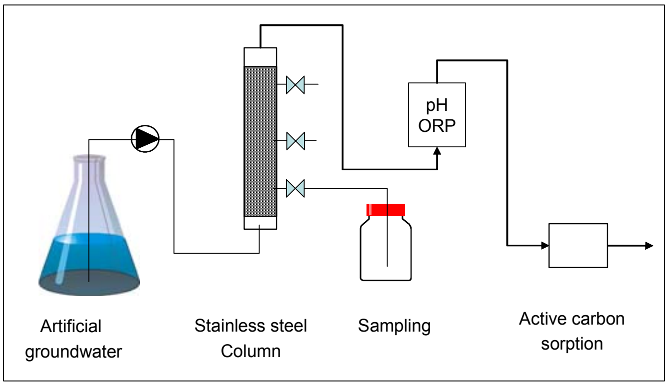


Figure 1 Schematic overview column experiments

The columns were filled with a mixture of compost, mulch, sawdust and woodchips originating from a Dutch composting firm (Table 1). The material will supply electrondonor for the anaerobic biodegradation and will also adsorb part of the HCH and the degradation products.

Composition of organic materials in the columns A and B

Table 2

Material	column A	column B
Mulch	40%	20%
Compost	20%	40%
Woodchips	20%	20%
Sawdust	20%	20%

Column A was filled with 4.1 kg of organic material and column B with 5.6 kg. Contaminated artificial groundwater was pumped through the columns with a standard flow of 2 L/d, resulting in a mean hydraulic retention time (HRT) of approximately 2.45 days for column A and 2.2 days for column B. The artificial groundwater solution was prepared with 100 µg/l HCH. The technical HCH consisted of a mixture of different isomers, with the alpha isomer being present in the highest concentration.

After three months, the longevity of the column materials was tested by flushing the column for one month with groundwater (without HCH) at a decreased HRT of 0.49 d (column A) and 0.44 d (column B) day. After this, the flow rate was restored to the original value of 2.0 L/d.

Zero valent iron

The batch study has been performed by the Belgian Research Institute VITO and consisted of two phases. In both phases, groundwater from the site was used to which technical HCH was added to obtain a final concentration of approximately 1,000 µg/L total HCH.

In the first phase, three different types of zerovalent iron (ZVI) were tested: granular ZVI, fine ZVI, and nanoscale ZVI. To batches containing 23 g (granular, fine ZVI) or 1.8 g (nanoscale ZVI), 110 ml of HCH-contaminated groundwater was added. In addition, a control batch without iron was started.

In the second phase only granular ZVI was used. The setup of the batches was the same as the first phase, but this time both the aqueous phase and solid phase (the iron) were analyzed to investigate the adsorption.

For the column experiments a glass column with a length of 1m and an internal diameter of 5.1 cm was filled with 5.0 kg of Gotthart Maier granular iron, grain size 300-300 µm. The granular iron was selected for its effectivity and hydraulic properties. The same artificial groundwater as used for the anaerobic column experiments was pumped through the column with an initial flow rate of 0.21 L/d. The hydraulic retention time in the column at this flow rate is five days.

Results

Anaerobic experiments

The results of the experiments are given in figure 2. In the anaerobic biodegradation experiments a HCH removal of over 90% can be achieved with a HRT of 2-2.5 day. With a HRT of 0.5 day approximately 50-60% of the HCH is removed. The measured biodegradation products (benzene, chlorobenzenes) can account only for a limited part of the HCH removal. Most likely sorption to the organic matter of the compost mixtures was continuously occurring, leading to the low yield of degradation products.

Zero valent iron

The results of the batch tests are given in figure 3.The batch tests have shown that ZVI can bring about a fast reduction of HCH with granular and fine ZVI. The reaction product is almost exclusively benzene. Using the aqueous phase data from the batch tests, an average half-life of 0.46 day can be estimated for total HCH. Furthermore considerable adsorption of HCH on iron was observed.

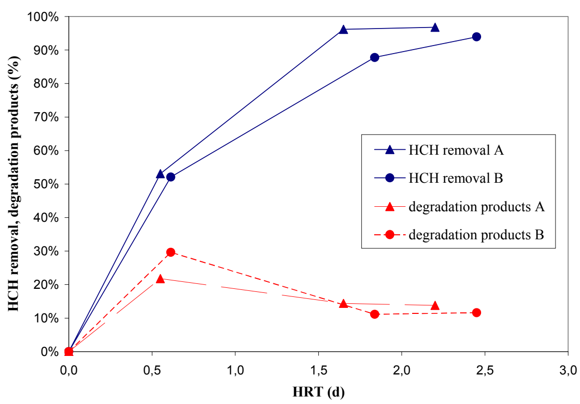
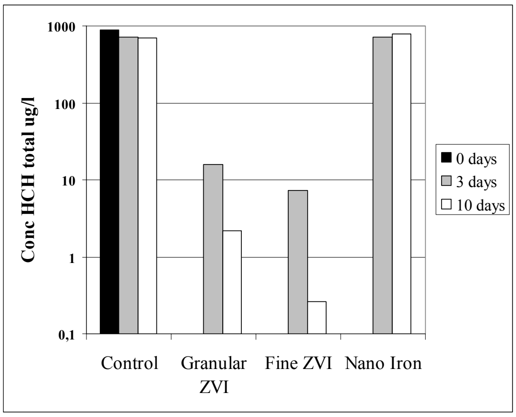


Figure 2. HCH removal and formation of degradation products (benzene and chlorobenzenes) at an influent level of 100 µg/l HCH and different hydraulic retention times (HRT) in column A and B after five months operation

Figure 3. Results of the batch tests



	control	ZVI		%
		water	solid	of total
	nmol	nmol	nmol	
alfa HCH	226,9	2,4	25,8	12,4%
beta HCH	192,9	0,4	7,9	4,3%
gamma HCH	52,9	0,2	4,6	9,1%
Sum HCH	472,7	3	38,3	8,7%
Monochlorobenzene	< dl	< dl	< dl	0,0%
123 Trichlorobenzene	< dl	< dl	1	0,2%
124 Trichlorobenzene	< dl	< dl	0,8	0,2%
135 Trichlorobenzene	< dl	< dl	< dl	0,0%
Tetrachlorobenzenes	< dl	< dl	< dl	0,0%
Benzene	< dl	173,2	237,2	86,8%
Mass balance				95,9%

In the figure the results of the experiments with different materials are presented; in the table a mass balance with granular ZVI is given.

The results of the column experiments are given in figure 4. In the first eight weeks of operation, the pH of the effluent was high (>9), which is a common phenomenon for ZVI. After the hydraulic retention time was decreased from five days to one day, the pH was somewhat lower with values of 7.5-8. The oxidation-reduction potential in the effluent was -200 mV during the experiment.

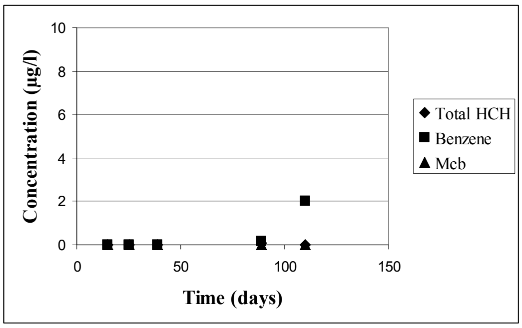


Figure 4. Results of the column experiments with zero valent iron at an influent level of 100 µg/l HCH and a hydraulic retention time of 1 day.

In the first 54 days, during which the hydraulic retention time in the column was five days, neither HCH nor its degradation products were detected in the effluent. After this period, the flow rate was increased to obtain a HRT of one day. Only after 89 days, at which time 41 pore volumes had been pumped through the column, low concentrations of HCH (0,08 µg/L)and benzene (0,14 µg/L) were detected in the effluent. At the last sampling moment, 110 days and 62 pore volumes after the start, HCH was once more below the detection limit (0,01 µg/L) and benzene was present in a concentration of 2 µg/L, accounting for only 7.5% of the HCH in the influent. Adsorption to the solid phase will have influenced the effluent levels.

Conclusions

The removal of HCH by treatment with chemical reduction on ZVI is a promising technology. Laboratory batch and column experiments have demonstrated that the treatment with ZVI can result in an almost 100 % removal of HCH from the groundwater. The treatment with zero valent iron is a treatment that quickly destroys the HCH-molecule. Based on the properties of the materials it is expected that sorption is an important process to consider, especially in the material containing organic matter. ZVI will adsorb less HCH and will therefore be more reactive than the organic matter. The cost effectivity of the process as compared to an anaerobic treatment with compost or adsorption on e.g. granular activated carbon will have to be determined on a site specific scale.

The degradation product of the ZVI reaction is almost exclusively benzene, which will have to be dealt with. Benzene is also a toxic compound, it has a higher mobility in the environment, but it has lower toxic properties compared to HCH. The low solubility of HCH combined with the weight loss of a factor 3 during transformation of the HCH molecule will lead to relatively low levels of benzene in groundwater. Furthermore it is widely known that benzene can be treated effectively by natural attenuation in aerobic aquifers, which are often present in the subsurface in countries where HCH was applied.

References:

1. Langenhoff, A.A.M., J.J.M. Staps, C.G.J.M. Pijls, A.Alphenaar, G.Zwiep and H.H.M. Rijnaarts (2002). Intrinsic and stimulated in situ biodegradation of hexachlorocyclohexane (HCH).- Water, Air and Soil Pollution 2, 171-181.
2. ITRC (Interstate Technology & Regulatory Council). 2005. Permeable Reactive Barriers: Lessons Learned/New Directions. PRB-4. Washington D.C.: Interstate Technology & Regulatory Council, Permeable Reactive Barriers Team.
3. RUBIN a Permeable Reactive Barrier (PRB) R&D network: http://www.rubin-online.de/english/i ntroduction/ index.html.

DECONTAMINATION OF HCH POLLUTED LANDS

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As a result of treating the soil with casual indifference, Romania has today many contaminated sites, some of them unidentified.

Article 66 of the Emergency Ordinance 195 / 2005 says that, in the very next future, the regulations regarding the modalities of investigation and evaluation of polluted soil, subsoil, terrestrial ecosystems, as well as the decontamination of polluted soil are to be established.

Aware that persistent organic pollutants (POPs) pose major and increasing threats to human health and the environment, in June 2004 Romania ratified by Law 261 / 2004, Stockholm Convention on POPs.

In April 2006 Romania sent the National Implementation Plan (NIP) to the Secretariat of the Stockholm Convention.

Concerning the contaminated lands in Romania, one of the most difficult situation is in the HCH (hexachlorocyclohexane - Lindane pesticide) polluted area near Turda town, Cluj county.

Here, one of the four emplacements of HCH existing polluted lands, namely the one which is located nearby the National Road number 1 – called DN 1 -, has been chosen for a decontamination demonstration project. The project has been approached by two versions: excavation and disposal of contaminated soil ex-site in a centralized controlled landfill (Version 1) and immobilization (Version 2).

The total surface area covered by all four deposits is 21,400 ha, of which the deposit chosen for the demonstration project (DN 1) is 5,000 ha. The total volume of all deposits is 32,700 m^3 (60,400 tonnes) of which DN 1 deposit is 7,500 m^3 (13,800 tonnes).

Under the first version a central deposit with the effective volume of 9,000 m^3, covering a surface area of 3,200 m^2, has been provided.

With the second version each existing deposits is to be isolated to avoid groundwater pollution.

Version 1 (with centralized deposit) has been estimated roughly to be 711,150 USD and Version 2 (isolation of each existing deposit has been estimated to be 1,101,900 USD).

For all four emplacements in Turda zone, the total cost has been established to be 2,220,000 USD – Version 1 and 2,700,000 USD – Version 2.

The investment in both Versions will last until November 2009 – for remediation of contaminated site and December 2012 for the period of operation and control.

Analyzing the technical proposals for Turda project it can be concluded that the first version excludes the environmental problems. Version 2 is more risky and more expensive regarding investment and O & M.Version 1 is quick and well documented.

KEY WORDS: contaminated soils, HCH, POPs, Stockholm Convention, decontamination solutions, project proposals.

1. Introduction

To address the important issues of POPs, in 2002 Romania requested and received a GEF Enabling Activity Grant through United Nation Industrial Development Organisation (UNIDO) to fulfill its obligations under the Stockholm Convention and prepare and endorse its National Implementation Plan (NIP) on Persistent Organic Pollutants. The final NIP was sent to the Secretariat of Stockholm Convention in April 2006.

Besides, an analysis of the HCH (lindane isomers) contaminated site at Turda in the county of Cluj is undertaken which has been ranked high on the list of priority contamination sites by the government, as well as in the NIP action plan.

HCH (Lindane) has been included in the List of POPs according to the decision taken with the second Conference of Parties (COP2) of Stockholm Convention. COP2 was held in Geneva in 2005.

There have been some previous studies elaborated for Turda. These studies are specified in the "References" chapter.

2. TURDA PROJECT - Decontamination of the Turda – HCH (Lindane) polluted site

2.1. General data

Emplacement: at the exit road from the town of Turda to Alba Iulia town at km 447 of the National Road DN 1 out of the living area of Mihai Viteazu village. The surface area is 5,000 m^2, that is 23 percent of the whole area covered by all four deposits in Turda zone. Regarding quantity, the DN 1 deposit has a volume of 7,500 m^3 of waste (13,800 tonnes), that is 23 percent of the whole volume of 32,700 m^3 deposited in Turda zone. Although each existing HCH deposit in Turda zone has a certain health risk this DN 1 deposit might deteriorate the quality of the groundwater used for water supply system in the zone.

Thereis agricultural land in the neighborhood of the proposed cleaning up land.

The land is in the ownership of the mayoralty.

The reasons for selection of this emplacement for the demo-project are:

- enough surface area available;
- the land is in the ownership of Mihai Viteazu mayoralty;
- there is an opportunity for co-financing. The high way investor is obliged to cover the cost of land used for the high way emplacement;
- the ground water table is deep (more than 10 m depth), that is the risk of groundwater pollution is reduced.

There are other three HCH (Lindane) deposits:

1. the emplacement located on the right side of Arieş River; this land is in the ownership of Turda Chemical Plant;
2. the emplacement of the Deposit S.C. “Constructorul” S.A. Cluj; this land is in the ownership of the company “Constructorul” S.A. CLUJ.
3. the emplacement of the Deposit “Poşta Rât” located on the former municipal deposit of Turda town, on the left side of the Arieş River. The municipal waste have been covered by dust of cement from the cement Turda factory. This emplacement is in the ownership of Forest Administration Company.

The representatives of the local Environmental Protection Agency (EPA) said that there would be other contaminated lands. These possible contaminated lands might not have been known up to now.

Project opportunity:

This project is included in the priority preventive measures at high risk sites to reduce human health exposure pathways.

This refers to the specific problems identified with the elaboration of the National Implementation Plan of the Stockholm Convention. There is not an exhaustive contaminated land inventory prepared up to now.

Soil contamination at Turda zone is caused by the HCH (Lindane) waste deposition. These wastes resulted from S.C. Chemical Plant Turda S.A., County of Cluj.

Turda Chemical Plant started producing Hexachlorocyclohexane 1, 2, 3, 4, 5, 6 gamma isomer since 1954. The active form was used as insecticide with the name of Lindane.

The product has been exported, in most part, to Japan. The applied technology produced an inactive gamma isomer. The quantity of waste (inactive gamma isomer) was 2.5 times the quantity of final Lindane sellable product. That is about 500 tonnes of waste per year. The production of HCH was stopped in 1983.

It was been estimated that a quantity of 15,000 tonnes of such waste has been deposited in Turda zone in the deposit DN 1.

Waste management was often rudimentary, which led to deficitary storage of HCH wastes and leakages from the waste deposits. Dangerous substances – HCH (Lindane) would seep into the soil for years.

The soil cleanup regulations are expected to be elaborated towards the end of the year of 2006 and that is why this project responds in time to the requirements of implementation of the Stockholm Convention on persistent organic pollutants, namely Hexachlorocyclohexane.

With the Conference of Parties held in Geneva in 2005, HCH has been included in the List of POPs.

2.2. Technical data

Emplacement and legal status of the land. Description of the activities on the emplacement

There are 4 emplacements of the existing deposits of HCH wastes from the Turda Chemical Plant, as it is shown in the study prepared by S.C. MINESA ICPM S.A. CLUJ NAPOCA.

a) The Arieş pond. The land (surface area, 4,000 m^2) is in the ownership of the chemical plant Turda (CF 11525 – topo 3181 / 1 / 2 and 3181 / 2 / 2). Now the company is in the final stage of legal wind up, according to the Law no 65 modified by Law 85. These proceeding has been started on 30.10.2000.

b) The deposit “Constructorul” SCCA Cluj – Turda working place. This deposit is located in the neighborhood of the chemical plant mentioned above ((a)) and covers a surface area of 2,400 m. The land is in the ownership of S.C. “Constructorul” SCCA Cluj.

c) The deposit “Poşta Rât” is located out of the living area of Turda town on the border line of “Poşta Rât” locality on the placement of a former quarry.

This deposit covers an area of 10,000 m^2 and is partially in the ownership of Turda forestry and partially to S.C. “Cimentul” S.A.

d) The deposit “DN 1”. This deposit is located out of Turda town, at km 447 of the national road Turda – Alba Iulia, DN 1. It covers an area of 5,000 m^2 and belongs to the locality Mihai Viteazu. This land is in the ownership of mayoralty Mihai Viteazu.

There is agricultural land in the neighborhood.

The Arieş pond is made in the embankment – between the concrete dam on the right side of Arieş River and the earth protection dam of the chemical plant. The deposit is a mixture of waste concentrated with HCH and inert materials and rubble. The uncontrolled deposit is leveled by means of bulldozers.

There are holes and ditches within the area of “Arieş pond” made by people commercializing illegally the residual products from the former chemical plant Turda.

There is no fencing, no watching and no monitoring of the HCH deposit. Rain water washes the HCH deposit transporting the pollutants to the surface water (Aries River) and groundwater in the respective catchments area.

The main characteristics of Aries deposit are:

- Surface area: 4,000 m^2
- The thickness of wastes: 2 m
- The thickness of earth closure: 0,3 – 0,5 m
- The volume of waste deposited: 8,000 m^3

The waste mass deposited: 14,800 tonnes.

The laboratory analyses have shown that the soil concentration in HCH exceeded the intervention threshold. The intervention thresholds value where the competent authorities may decide upon elaboration of risks evaluation studies and reduction of these emissions. These value limits are indicated by the Government Decision 756 / 1997.

The intervention thresholds mentioned by GD 756 / 1997 are:

- for PCB 28 and 52: 0.01 mg / kg
- for other PCB: 0.04 mg / kg
- for HCH: 0.5 mg / kg

The HCH concentration value was 472.9 mg / kg of soil.

The groundwater level has not been met up to 2 m depth.

The deposit “Constructorul” SCCA Cluj – Şantier Turda” is delineated in the precinct of the company “Constructorul S.A.”. It was fenced by a concrete wall which was deteriorated in the main part of its length. This allows the free access of the population in the zone.

The deposit “Constructorul SCCA Cluj – Şantier Turda” has the following characteristics:

- Surface area: 2,400 m^2
- The thickness of wastes: 3 m
- The thickness of waste closure: 0.3 – 1.0 m
- The volume of HCH waste – rubble mixture deposited: 7,200 m^3
- The mass of waste (white powder) deposited: 13,300 tonnes
- Groundwater table in the deposit zone: 3.7 m under the ground level
- The lithological strata succession in the deposit is:

- compacted clay;
- pebble and sand;
- sandy brown clay;
- HCH waste and;
- Soil.

The laboratory analyses have shown that the values of HCH concentrations exceeded the intervention value. The maximum HCH value was 884 mg / kg of soil.

The deposit “Poşta Rât” has been arranged on the former municipal waste deposit of the Turda town. The municipal wastes have been covered with cement and sterile powder from the Cement Factory – Turda. This deposit was emptied / flushed out by Arieş water during the flood which took place in 1970 – 1975. After these events the deposit was filled out with argillaceous wastes from Turda Cement Factory.

Although these are no hydraulic structures made for defense against flood the HCH deposit has been emplaced on the left side of Arieş River in its major streambed being always exposed to flood.

The deposit has not been planned in a certain way of land filing, so the waste has been thrown out, by random, in heaps. There was not an organized system of HCH waste deposition.

The "Poşta Rât" deposit is crossed by the River "Sărat" (alias Harcom) which flows from Salty Baths Turda.

This river has not controlled flow and sometimes change its course, flooding the area.

The main characteristics of "Poşta Rât" HCH deposit are:

- Surface area: 10,000 m^2
- Volume of mixture HCH waste – rubble: 10,000 m^3
- Weight of mixture HCH waste – rubble (white powder): 18,500 tonnes

The analyses have shown the HCH concentration value exceeded the intervention threshold. The maximum concentration value of HCH in soil analyzed was 345,3 mg / kg of soil.

DN 1 Deposit

It is located on the exit road from Turda town to Alba Iulia town at km 447 of the national road DN 1.

The land covers an area of 5,000 m^2, being delineated by DN 1 and agricultural lands.

Initially the waste deposit was closed by clay and inert soil.

People used to dig in the deposit area taking out material for selling as pesticide out of control.

That is why the actions to eliminate this effect are urgently definitely needed. The main characteristics of the deposits are:

- Surface: 5,000 m^2
- The waste deposit thickness: 1.5 m
- The waste deposit is covered by a stratum of inert soil – 0.3 – 0.5 m – thickness.
- The total waste weight is estimated to be 13,800 tonnes – white powder (volume – 7,500 m^3).
- The litho logical structure consists of sands, clay, compacted HCH waste and soil.
- No groundwater has been met with the soil logs which were drilled. That means that the depth was more than 10 m. This means that a controlled landfill deposit may be constructed (Romanian legal act – MO 757 / 2004 says that the deposits may be constructed at least 1 m above the groundwater table).

The HCH maximum concentration is 815.7 mg / kg of soil.

HCH waste deposits in Turda zone

Table 2.1.

Deposit name	Surface area (m^2)	Volume / Weight (m^3) / tonnes)
"Arieş pond"	4,000	8,000 / 14,800
"Constructorul"	2,400	7,200 / 13,300
"Poşta Rât"	10,000	10,000 / 18,500
DN 1	5,000	7,500 / 13,800
TOTAL	21,400	32,700 / 60,400

Geographical characteristics of the emplacement land

The contaminated lands are located in the town of Turda and around it. The emplacements are located in the southern part of the county of Cluj.

The county is situated in the North-West part of Romania.

Geologically the land belongs to Sarmatian era (sands, clay, slates, pebbles slightly cemented with intermediate strata of gypsum).

The relief of the zone of contaminated land consists of alluvial plain and terraces.

The river flowing in the area is Arieş with an average flow of 20 m^3 / s.

The climate is of moderate continental type. The annual average temperature is 8.4^{0}C. Rainfall has average values of 120 mm / 24 h and 600 mm / year. The dominant wind direction is N – W (12,8%) and W (10,4%). The average wind speed is 4 m / s. The annual average solar radiation is 115 kcal / cm^2.year. There is alluvial soil, in general specific for pastures and hay field.

Vegetation along the Arieş river valley consists of typical plant for waterside – hayfield and pastures.

The typical fauna in the forest areas consists of goat (Caprioles), lynx (Lynx), squirrel (Sciurus vulgaris), pheasant (Phasianus calchicus) and fish: grayling (Thymallus thymallus) and broad snoot (Chandrastoma nasus).

2.3. Project description

2.3.1. Objective: HCH polluted soil cleanup

2.3.2. Works:

- Preliminary site study;
- Further studies;
- Choosing a cleanup method;
- Drawing up the cleanup plan;
- Implementing the cleanup plan.

2.3.3. Preliminary site study has already been done.

The information about the history of sites and researches on the effects of HCH waste deposition have been performed. Soil sample have been taken and analyzed in the laboratory.

Passive air samplers have been installed. The sensitivity of measurement is according to the analytical method used for air quality analysis (at the level of 0.1 nanograms per cubic meter).

2.3.4. Conclusions of the preliminary site study

♦ Soil contamination by HCH (Lindane) has been observed. The soil analysis shown the exceeding of the maximum intervention value. The concentration value of soil is between 345.4 and 884 mg / kg.

The intervention threshold value provided by the Government Decision 756 / 1997 is 0.5 mg / kg of soil.

♦ The contaminated land covers a surface area of 21,400 m^2 (32,700 m^3, namely 60,400 tonnes), in total; there are 4 main contaminated lands in Turda zone: Arieş pond, “Constructorul”, “Poşta Rât” and DN 1. But other contaminated sites might be detected as it was declared by the officials from the County Council, mayoralties and environmental local authorities.

♦ Soil contamination in those four emplacements in Turda zone has been caused by intentionately deposition of waste produced in the Turda chemical plant producing HCH (lindane) in the former time.

♦ The proposed demonstration project is related only to DN 1 emplacement. This solution has been chosen based on the following reasons:

– enough big surface area available;

– the land is in the ownership of Mihai Viteazu mayoralty; in consequence, there will not be complications related to the land acquisition;

– opportunity for the project co-financing by the high way investor (the high way which is to be constructed crossing the respective emplacement);

– the groundwater table is located deeper than 10 m under the ground level, so the deposit could be installed taking the depth of 10 m depth. This means that the total volume of deposition could be taken as 5,000 m^2 surface x 10 m (depth) = 50,000 m^3, that is more than 32,700 m^3 – the total effective volume of the future deposit installed at DN1 emplacement (if the central deposit will be in the zone of existing HCH deposit DN 1).

2.3.5. The further study

The further study is intended to produce a complete picture of seriousness and scale of contamination, and a certain how urgently it needs to be cleaned up. It also solves the following problems:

- to define more accurately the places where contamination occurs;
- to specify whether HCH (Lindane) pollutant has spread to the environment;
- to specify the danger posed by HCH pollutant to human beings, animals, or plants.

For further study comes in two parts: the first part aims to determine the scale and concentration of the contamination, and the second part consists of risks analysis.

There have been some previous studies elaborated for Turda. These studies are specified in the "References" chapter.

For Turda the technical solution proposed consisted of providing a central deposit. This deposit was proposed to be located on the river side Arieş, where it was the former deposit of the chemical integrated plant Turda.

This is an improper emplacement to be proposed because:

– it is located near by the river Arieş. At present, Law of Waters (107 / 1996 and 310 / 2004) does not allow that.

– the land is not in the ownership of the state.

2.3.6. The cleanup method

Once a cleanup method is chosen a cleanup plan is to be drawn up.

Two samples are chosen before full assessment of the optimum method for cleaning up soil in Turda zone:

1) Excavation and disposal of contaminated soil ex-site at a controlled landfill
2) Immobilization

Version 1) has the following advantages:

a) more availability – that is less complications for investments and consequently, cheaper solution and less time for achieving the objective;

b) possibility of extension for receiving other hazardous wastes under controlled conditions.

Version 2) has the advantage of acting in situ

Although there are four emplacements with contaminated soil at Turda zone, only one emplacement is considered for this demonstration project, namely, DN 1.

The demo project is evaluated as such. The demo project will be extendable for other polluted emplacements. The situation plan of the emplacements in the zone is shown in Figure 2.1.

ADN 1 emplacement has been chosen due to the following criteria:

- no problem regarding the ownership of the contaminated land; the land is in the ownership of mayoralty;
- no problem with the groundwater table;
- there is an "easy" access road to the emplacement;

more opportunity: the European highway Braşov – Borş goes across the proposed emplacement, so the co-participation of the Ministry of Transportation is expected to be most probably.

2.3.7. Project description

<u>Version 1</u>

The contamination is removed by excavators under controlled conditions, until the sides and bottom of the excavation are sufficiently clean. The extracted contaminated soil is to be replaced by clean soil transported from a borrow pit.

The new central deposit will be constructed in 16 compartments.

Each compartment will have an effective volume of 3,000 m3. So, in total the effective volume will be 48,000 m3. In the first stage only the compartments for DN 1 emplacement will be built, namely those necessary to landfill 7,500 m3 corresponding to the demo-project.

Three compartments with effective volume of 3,000 m3 each will be provided. The dimensions of each compartment are:

˜ length – 60 m,
˜ width – 10 m,
˜ depth – 7 m (total) and 5 m (effective).

The total surface area in demo-project phase is 40 x 80 m = 3,200 m2.

The scheme of insulation of each compartment is shown in Figure 2.2.

The excavation is to be documented using analysis of soil samples taken from the sides and bottom of the excavation. For excavation the control phase is concomitant with the remedial phase.

The central deposit will be insulated in such a way that no environmental effects will exist. To be sure on this, observations wells will be placed around the deposit and groundwater will be monitored during 30 years time after the final closure of the deposit. The contaminated soil will be covered according to the indications in Figure 2.2. Turf will be planting (no tree will be planted to disturb by their roots the impervious closure).

Facilities will be organized (watching gate provided with heating, electricity water supply and sewage.. The central deposit will be fenced and warning plates will be placed on each side.

The advantage of the method is that it is quick and well documented.

– existing deposits
- 1. Aries Pond
- 2. “Constructorul”
- 3. “Posta Rat”
- 4. DN1

– new proposed central deposit

Figure 2.1 Land decontamination at Turda zone: layout plan

<u>Version 2</u>

This version consists of immobilization. The contamination is fixed, so that the polluted area could be insolated.

The contamination is sealed by having membranes made of synthetic materials (similar to Version 1).

“Vertical sealing” is to be applied to prevent horizontal spread of contamination by using membranes in the excavation opened. Laying membranes are supplemented for collecting and draining precipitation.

The precipitation solution applied is explained in Figure 2.3.

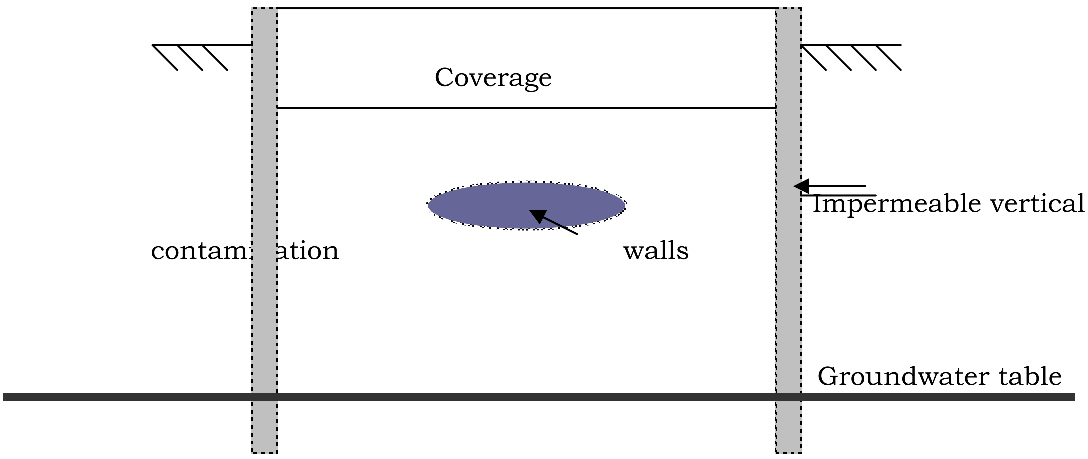
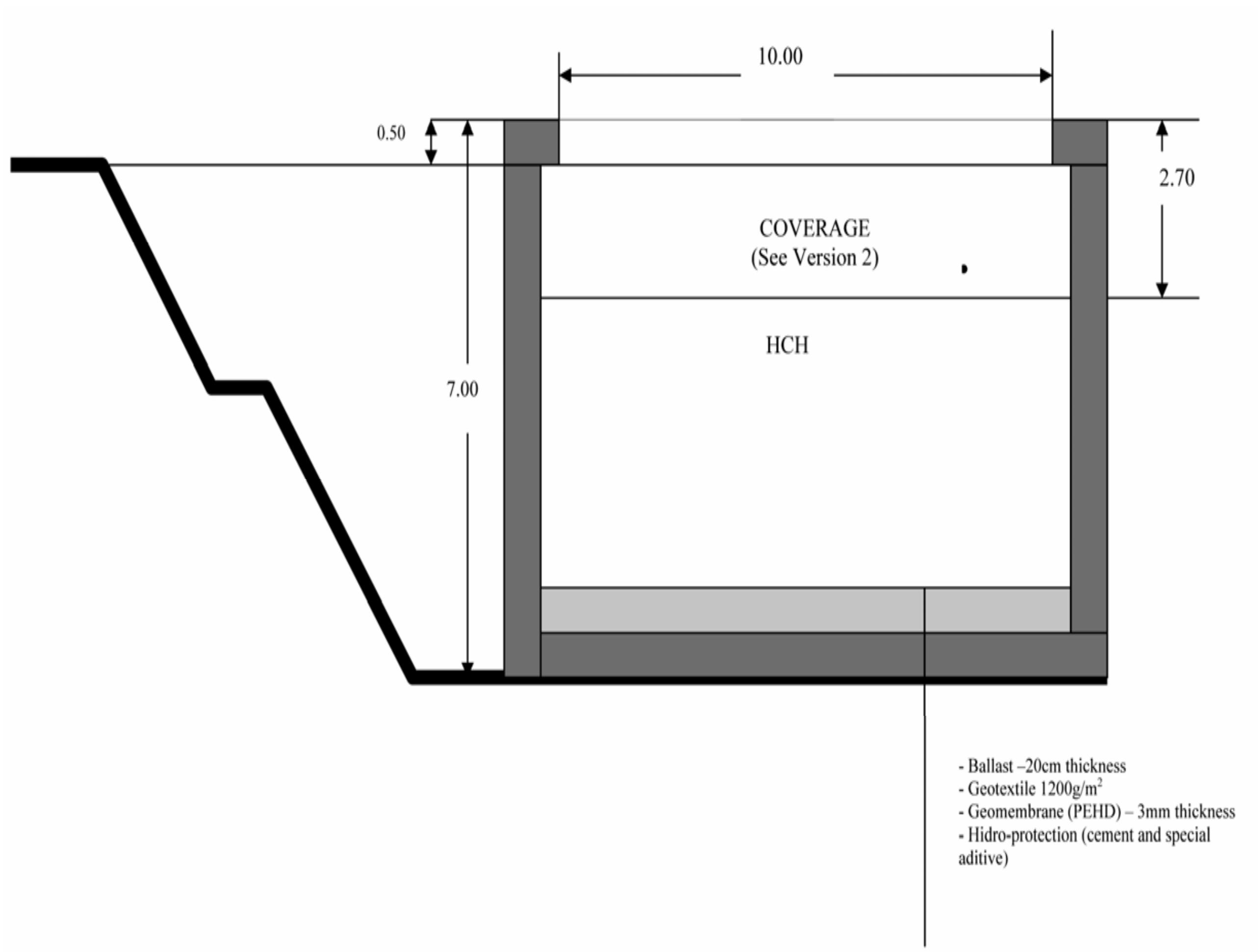


Figure 2.2. Version 2: sealing contamination

Figure 2.3. Deposition compartment: Cross section



The coverage consists of the following layers:

- supporting layer (50 cm of soil);
- impervious layers of clay (2 strata of 25 cm each);
- insulated membrane (PEHD of 2 mm thickness);
- geotextile for membrane protection (> 600 g / m^2);
- drainage layer (40 cm – thickness);
- geosynthetic layer (geotextile – polyethylene (400 g / m^2);
- argillaceous soil with sand (1.0 m thickness);
- clean soil (30 cm in thickness);
- turf.

This version is more risky with the effects on environment and requires more personnel and facilities. Instead of a central deposit which could be more easily controlled, 4 emplacements are to be maintained and operated.

Observation wells are to be constructed in 4 areas instead of one area after the final closure of each deposit.

2.4. Cleanup plan

2.4.1 Main activities and related costs

♦ Study and analysis previous field surveys, feasibility study conducted sampling and monitoring data. Of particular importance is the feasibility study in order to determine the need for more detailed site investigations prior to design works.

♦ Collection and analysis of necessary geological, topographical, hydrogeological and other data, including execution of identified and agreed additional sampling and testing programs and Environmental & public health risk assessments, identification of primary low cost actions.

♦ Analysis of alternative options and preliminary assessment on technical solution with Client based on basic remediation design and preliminary costs estimate.

♦ Preparation of Detailed Remediation Design, including drawings, including operation and maintenance plan.

♦ Preparation of Bidding Documents, Procurement Assistance.

♦ Training and Transfer of Skills.

Total cost for cleaning up all contaminated land in four emplacements in Turda zone is estimated 2,220,000 USD, of which the investment is 2,120,000 USD – in the first Version and 3,100,000 USD, of which 2,700,000 USD the investment – in the second Version.

The total cost for the 4 emplacements has been calculated by taking into consideration the following aspects:

- the volume of the excavated soil for each emplacement for earthworks;
- by extrapolation according to the size of the surfaces of each contaminated land for fencing, sidewalk arrangements, impermeable walls, final coverage – multiplying the calculated unit cost by the surface area.
- works like obtaining land licenses, expenses for designing and technical assistance, organization and legal taxes, training and public awareness have been evaluated multiplying the value obtained for DN 1 by 4.

2.5. Conclusions

1. Version 1 consists of the excavation the HCH wastes from the existing deposits and transferring it to the new controlled deposit. This technical solution excludes the environmental problems.

2. Version 2 consists of the isolation of each of the existing four deposits of HCH in the zone.

3. Comparing these two versions the first version is more advantageous due to the following reasons:

▪ Version 2 is more risky because instead of one place to be controlled, there are 4 places which could present a potential danger to the environment;

▪ Version 2 is more expensive as far as the investments and operation and maintenance expenses are concerned. This difference between Version 1 and Version 2 is amplified by the difference appeared when the extension of the demo project (cleaning up of DN 1 Turda site) is taken into account: 711,150 USD – Version 1 and 1,101,900 USD – Version 2 (these costs comprise investments, operation and maintenance costs);

▪ The advantage of method 1 is that it is quick and well documented;

In consequence Version 1 is recommendable.

References:

1. The Research and Designing Institute for Mines S.A. – MINESA – “Prefeasibility study for ecological reconstruction of the emplacements of the existing deposits of HCH belonging to the Turda chemical plant in the county of Cluj, 2004”.
2. The National Research and Development Institute for Environment Protection – “National Implementation Plan for Stockholm Convention, 2005”.
3. Scientific Equipment Centre – CAST Bucharest – “Environment Assessment”, 2001.
4. COUNTY COUNCIL OF CLUJ – “Prefeasibility study on municipal and industrial waste management in Turda and Câmpia Turzii zones, 2001”.
5. S.C. AMT SERVICE – “Report on emplacement evaluation and environment impact assessment”, 2005.
6. JICA – “Final Report” – Vol. 1 and 2, Vol. 3, Chapter 5 and Vol. 6.
7. OBREJANU GR. – « Metode de cercetare a solului », Editura Academiei, 1964
8. Environmental Science & Technology – « Sommaire des criteres relatifs aux biphenils polyclores (PCB) dans l’environment » - Canada, 1987.
9. Environmental Science & Technology – « PCB: Questions and Answer Guide Concerning Polychlorinated Biphenyls” – Canada, 1981.
10. World Bank – “Environmental management loan activities”.
11. GEF MSP – “Project to strengthen Romania’s national capacities for managing the PCB-issue in an environmental sound manner”.
12. GEF Council Submission – “POPs Management and Destruction Project (Moldova) ID PO 90037.
13. Ministry of Environment and Water Management – “Implementation Plans for EU Environmental Directives (eg Council Directive 96/59/EEC on the disposal of polychlorinated biphenyls and polychlorinated terphenyls, PCBs/PCTs).
14. The National Strategy for Waste and Hazardous Waste Management and the National Action Plan for Waste Management.

REMEDIATION OF THE SPOLANA NERATOVICE

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The aims of this study was focused on and the using of this simple tool for the study and evaluation of real environmental effects of industrial source where the direct effects of the chemical technology is combined with the old environmental burden and ongoing remediation of this site. As a model case was selected Spolana Neratovice in the Czech Republic, where remediation of a part the factory area was started in 2005. The POPs in the surroundings of remediation site, where BCD non-combustion technology is deployed, are evaluated using by polyurethane passive samplers.

Keywords: POPs pesticides, former production, remediation, monitoring of remediation.

Introduction

The Spolana chemical site is a large chemical complex based on chlorine chemistry in the Czech Republic. This chemical factory is situated approximately 25 km north of Prague at the Elbe River. During the 1960s, the production unit called PCP (pentachlorophenol) produced insecticides and herbicides. It also produced in the period of 1965-68 the chlorine herbicide 2,4,5-T and chlorinated phenols. A part of 2,4,5-T was even exported to the USA and was applied as the component of "Agent Orange" within the Vietnam war. During the production due to breaking technological conditions, a huge amount of dioxins (in particular, the most toxic 2,3,7,8-TCDD) was formed and former factory buildings containing products, intermediates, installations, etc. belong currently to the most dioxin-contaminated sites on the globe. Moreover, soil in the factory is highly contaminated with organochlorine pesticides produced there, as well. The 2,4,5-T and chlorophenols production was stopped in 1968 when about 80 cases of occupational diseases developed (55 workers were hospitalized mainly with severe chloracne manifestations and porphyria [1].

Chemical analysis proved an extremely a high degree of the contamination of waste products stored in production buildings, building walls and floors, air, soil and ground water. The highest concentration of dioxins (over 24 ppm of 2378-TCDD) was measured in the residues of chemical substances. It is assumed that there are tons of these waste stored in the buildings. The immediate toxic impact of dioxins in the air of the contaminated buildings was proven by a rabbit experiment in the 1970s. Rabbits in cages were located in the buildings to be exposed only to dioxin-contaminated air. The rabbits started to die on the 7th day of the experiment. Autopsy showed a significant damage of the liver, lung and kidney.

A lot of risk analyses and studies, which were performed after 1989, have confirmed the extremely high level of contamination and classified this area as old environmental burden.

The Spolana factory including some of the dioxin-contaminated buildings was flooded in 2002 and one can expect dioxin release into agricultural fields and Elbe River and its sediment. An extended of environmental contamination was mapped in detail without delay as well as to start with the definitive solution of dioxin-contaminated buildings and soil in their vicinity in Spolana Neratovice [1].

The remediation of site

The decontamination and remediation of site started after very complicated procedure at 2005 with using of base catalysed dechlorination non-combustion technology. These processes consist from the decontamination and demolition of 2 buildings (9 000 tones of wastes), excavation and treatment of surrounding soils of these two buildings (23 000 tones), treatment of chemicals stored closed to main building (160 tones), dissemble and treatment of the process unit (3 000 tones of metals) and backfill and final restoration.

The main requirements for the process of decontamination and remediation were the treatment of contaminated waste in site, final destruction of toxic waste, use of non incineration technology, use of proven technology, protection of environment, safety and health for population. All these steps are monitored by the sampling and analytical methods which respect the international standard and procedures.

The BCD technology was selected by the Czech Ministry of Environment for the deployment in this case. From the emission point of view, two main aspects of the deployment of BCD technology are follows. Firstly, the main bulk work done by the BCD plant is the treatment of cyclone dust and filter cake from the ITD off gas filtration, both of which are mainly mineral dust from the treated soil and represent the ultimate destruction of the contaminants stripped from the soil by thermal desorption. Secondly, the products of a BCD reaction are process oil and the solid residue from the reaction. The oil is recycled in its entirety and as such it does not strive for complete destruction. The solid residue from the BCD centrifuges, are submitted to a further thermal treatment to recover the residual oil in the centrifuge cake. In this process too any residual contaminants are stripped from the sludge.

Company does not strive in this operation for complete destruction, but a significant reduction so that they are sure there is no accumulation. It is a possible to increase the severity of the reaction conditions. The reason they do not do this is to get maximum recycling of process oil, since more severe conditions lead to a faster reduction of the flash point of the oil. At low flash point company disposes of the oil, dioxin free, off-site and destroys usually by combustion. Only recent chemical wastes are also treating, since the low contaminant values in the mineral cake and dust do not demonstrate. The chemicals are treated on an irregular basis, as they are recovered from the different phases and area of the buildings decontamination.

The study of effects of source and the impacts of site remediation

Air monitoring for POPs has conventionally been conducted at a very limited number of sites using 'active' or high volume air samplers. These are expensive, require electricity and a trained operator. Regulatory and other developments mean there will be a pressing need to obtain more POPs data for air, in a much more routine and cost-effective way, to ensure compliance. This provides the incentive to develop new and cheaper passive air sampler (PAS) options. Passive air sampling as a cheap and versatile alternative to the conventional high volume air sampling is one of the methods currently considered as suitable for the purpose of such monitoring programmes [2,3].

National Environment Agencies increasingly need to identify 'less obvious' diffusive sources of POPs, as they seek to further reduce emissions, now that more obvious primary sources have been/are becoming better controlled. PAS can be used to conduct 'screening/reconnaissance surveys', and are sensitive to site-/source-specific compound fingerprinting. They can therefore be used to help identify sources, and be used to help direct/target cost-effective active air sampling campaigns [4,5]. Feasibility of obtaining such data on seasonal variations in ambient air concentrations of persistent organic pollutants on the local scale using the passive air samplers, was studied very intensively [4].

RECETOX studies confirmed that they are sensitive enough to mirror even small-scale differences, which makes them capable of monitoring of spatial, seasonal and temporal variations. Passive samplers can be used for point sources evaluation in the scale of several square kilometers or even less – from the local plants to diffusive emissions from transportations or household incinerators – as well as for evaluation of diffusive emissions from secondary sources. While not being sensitive to short time accidental releases passive air samplers are suitable for measurements of long-term average concentrations at various levels [4].

Very good capability of passive air samplers to reflect temporal and spatial fluctuation in concentrations of persistent organic pollutants in the ambient air was confirmed by our studies. While this sensitivity makes them suitable for the monitoring of local sources, it also needs to be considered when designing large scale monitoring networks.

Results and Discussion

The remediation of the chemical factory including the buildings heavily contaminated with pesticides and dioxins, and contaminated soils started in 2006. BCD (Base Catalytic Destruction) technology selected for the task has been operated in the tent and was not supposed to have any impact on surrounding environment. However, an extensive field work including a relocation of contaminated soils was a part of the project. Available data from above mentioned study performed before the remediation enabled an estimation of direct impact of the remediation processes as well as verification of an improvement of the surrounding air quality in the long run, when the remediation activities are completed. Results of the first task were summarized separately in the scientific report from this specific case study [6]. In short, remediation activities caused significant (up to 1.5 order of magnitude) increase of the POP contamination of the ambient air both, within the factory, and in neighboring residential areas. This contamination, however, dropped back as soon as the field works with contaminated soil was terminated. Second part is still in progress, a significant decrease of OCP atmospheric concentrations in the area is expected in following years.

Up to ten parallel PUF passive air samplers were deployed in the area and vicinity of the Spolana Neratovice since the 2004. The polyurethane filters were exposed for 28 days. The samples collected on each site were analyzed for PAHs, PCBs, OCPs [4]. The aims of this study was focused on and the using of this simple tool for the study and evaluation of real environmental effects of industrial source where the direct effects of the chemical technology is combined with the old environmental burden and ongoing remediation of this site. The first results were published recently [4].

Very good capability of passive air samplers to reflect temporal and spatial fluctuation in concentrations of persistent organic pollutants in the ambient air was confirmed in this study. While this sensitivity makes them suitable for the monitoring of local sources, it also needs to be considered when designing large scale monitoring networks.

In the case of the Spolana Neratovice, a point source of secondary air pollution in mainly the volatilization from contaminated soils and contaminated buildings. Figs. 1 and 2 show the levels of HCHs and DDTs respectively, in the area and in the vicinity of the factory including the spatial distribution of HCHs and DDTs around the factory and comparison with some other sites. These sites are a part of the Czech national POPs ambient air monitoring which is operated by the RECETOX.

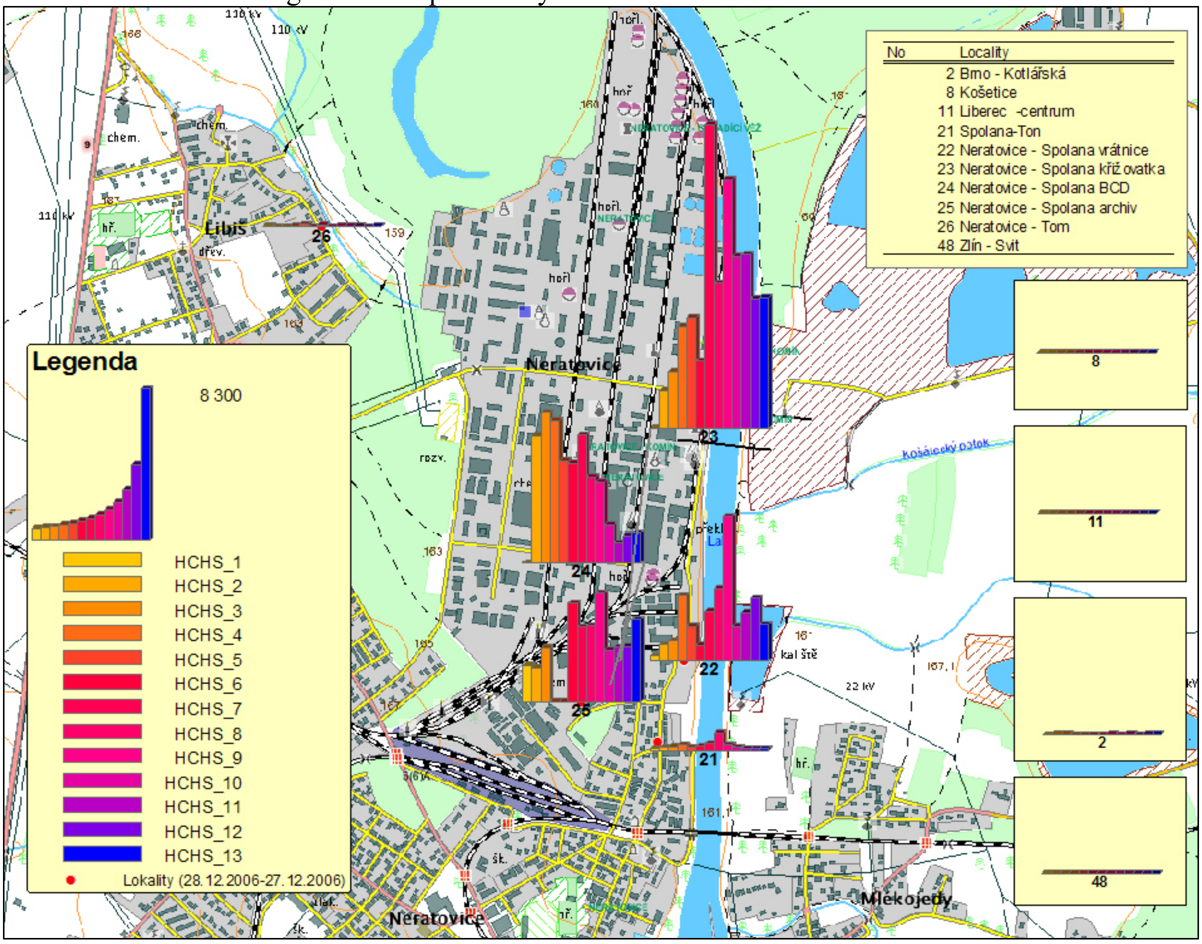

Figure 1: The comparison of the HCHs levels in the area of Spolana Neratovice with the levels nearby factory and some other site in the Czech Republic
(x-axys – months of sampling; y-axys – the level of HCHs [ng/filter])

This study suggests the passive samplers are sensitive enough to mirror even small-scale differences, which makes them capable of monitoring spatial, seasonal and temporal variations. Passive samplers can be used for point source evaluation in the scale of several square kilometres or even less from the local plants to diffusive emissions from transportations or household incinerators as well as for evaluation of diffusive emissions from secondary sources.

The deployment of these samplers also clearly shows the potential impacts of the industrial source on the vicinity nearby this source. The differences between the levels of HCHs in the area of the factory and the levels in the nearby surroundings are high and confirm that the impacts of the industrial sources could not be as dramatic as is a usually described.

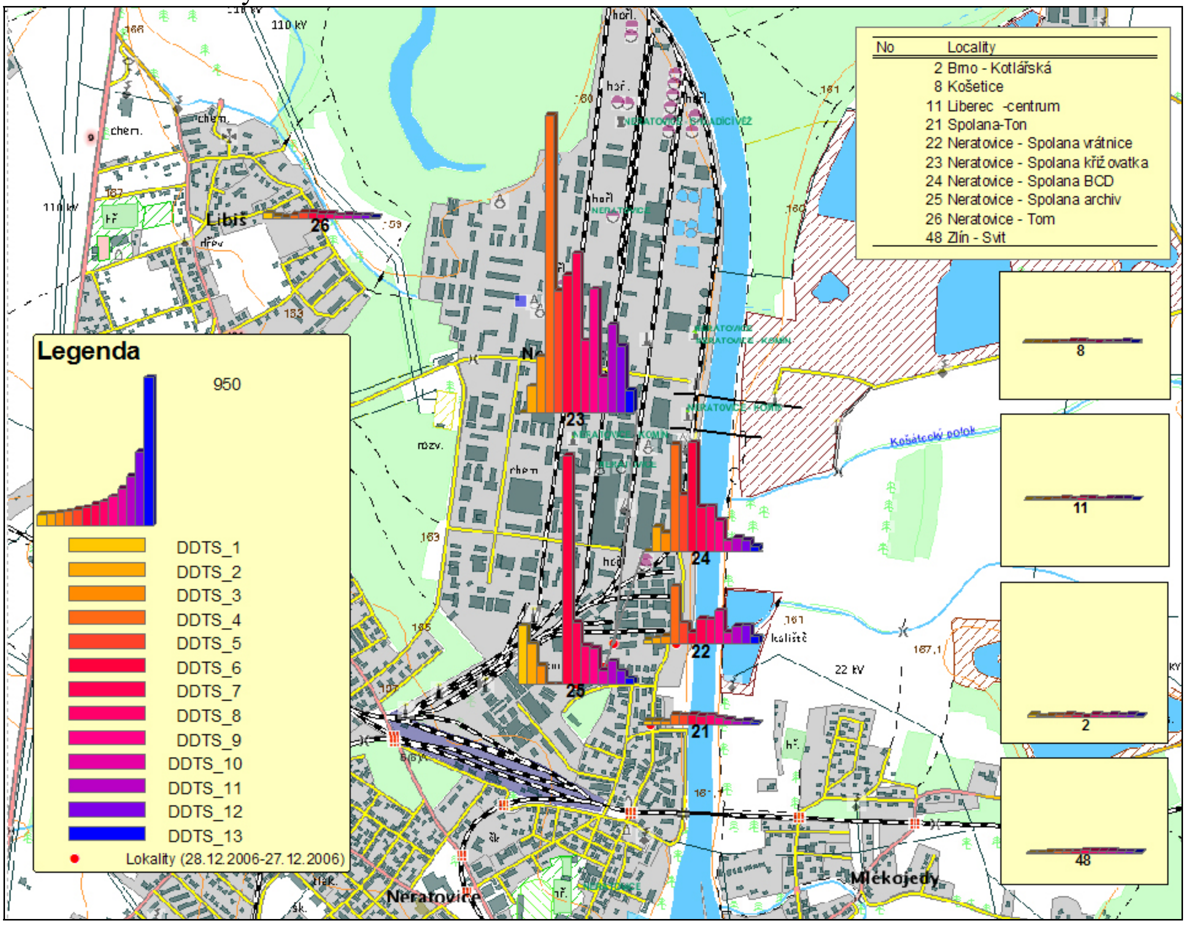

Figure 2: The comparison of the DDTs levels in the area of Spolana Neratovice with the levels nearby factory and some other site in the Czech Republic (x-axys – months of sampling; y-axys – the level of DDTs [ng/filter])

Acknowledgements

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References:

1. Holoubek I, Čupr P, Jech L, Ocelka, T, Kužílek V, Vácha R, Škarek M, Matoušek J, Kočan A. *Organohal. Compds.*, 2003; 61:353.
2. UNEP Stockholm Convention, United Nations, New York and Geneva, 2001
3. Harner T, Bartkow M, Holoubek I, Klanova J, Sweetman A, Wania F, Jones K.C. *Environ. Pollut.* 2006; 144/2:361. (2006).
4. Klánová J, Kohoutek J, Hamplová L, Urbanová P, Holoubek, I. *Environ. Pollut.* 2006; 144/2:393.
5. Čupr P, Klánová J, Bartoš T, Flegrová Z, Kohoutek J, Holoubek I. *Environ. Pollut.* 2006; 144:406.
6. Holoubek, I.; Klanova, J.; Čupr, P. "Sledování stavu znečištění složek životního prostředí persistentními organickými polutanty v okolí Spolany Neratovice (2006). RECETOX-TOCOEN REPORT No. 303," Masaryk University, 2006.

APPLICATION OF BIOREMEDIATION TECHNOLOGY FOR DETOXIFICATION OF HERBICIDE/DIOXIN AND DDT CONTAMINATED SOILS

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Introduction

In order to find out the suitable resolution for detoxification of POP contaminated sites in Vietnam we conducted our research on bioremediation technology and particularly using several technologies: isolation, absorption together with bioremediation that named "Active landfill" and only aerobic degradation by the use of bioreactor. Field trials with different scales for detoxification of contaminated site in South Vietnam were carried out [1-5] and pilot scale for DDT, HCH contaminated soil was also studied. Our technology based on stimulation of indigenous dioxin and toxic compound-degrading microorganisms of heavy POP contaminated site by providing them suitable condition as well as necessary sources for their activity in oxidation, reductive dechlorination and catabolic processes.

For heavily contaminated herbicide/dioxin soil of former Danang US military base bioremediation technology was applied in field trails of 'hot spot'. Site sandy soil contaminated with not only with 2,3,7,8-TCDD (from several thousand to hundreds thousand ppt) but also with big amount of other toxicants such as 2,4,5-T, 2,4-D, TCP, DCP and PAHs. Different in situ scales of bioremediation treatments were conducted, ranging from 0.5, 1.5, 10 to 100m^3 in 'Active Landfill' cells in Da Nang former military base. Recently, new approach for detoxification of pesticide contaminated soils was developed. By the use of 100 kg aerobic bioreactor, bioaugmentation treatment at pilot scale was investigated.

Result

Herbicide/dioxin degradation in biostimulation treatment

In this paper we demonstrate some results from one (1.5DN5) of 13 treatments that were studied in field trail.

Microbial number and diversity

Microbial enumeration was carried out 9 times at starting point (before treatment), 2,4,6,10,15,18,22, and 24 months. Before treatment only heterotrophic bacteria could detected with low number x10^3 MPN/g soil and filamentous fungi x10^2 CFU/g soil. This group of microbes increased 100 – 1 000 000 times during 9 month microbial analysis (Fig.1A).

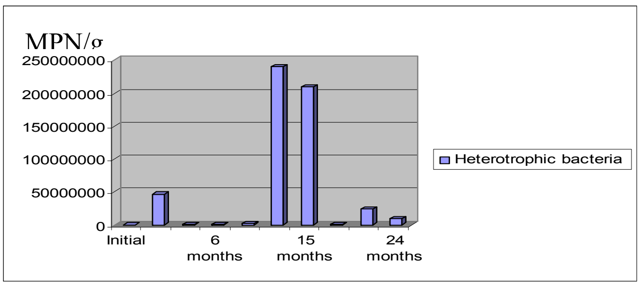

Figure 1: Number of heterotrophic bacteria in 1.5DN5

Actinomycetes and yeasts were not detected in all samples, except low number of actinomycetes was found in 18 month treated sample. Filamentous fungi almost found with increasing number from x10^3 to x10^5 CFU/g soil in 2, 4, 6, 15, 22, month samples and decreased in 10 and, 18, month samples.

This group of microorganisms was not found in 24 month sample when water was completely filled in the treated tank. Nitrate and sulfate reducing bacteria were detected from x10^2 to x10^7 MPN/g soil in almost examined samples. The enumeration of sulfate reducing bacteria describes in figure 1C. Two other kinds of anaerobes cultivating in the media with soil extracts appeared only in few samples with low number, in the 24 month sample, bacteria were found at high number x10^7 MPN/g soil.

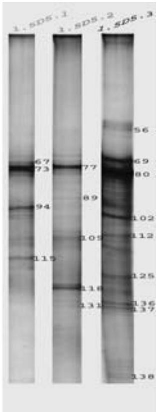

Figure 2A: PCR – SSCP community profile of 1.5 DN5 biotreatment

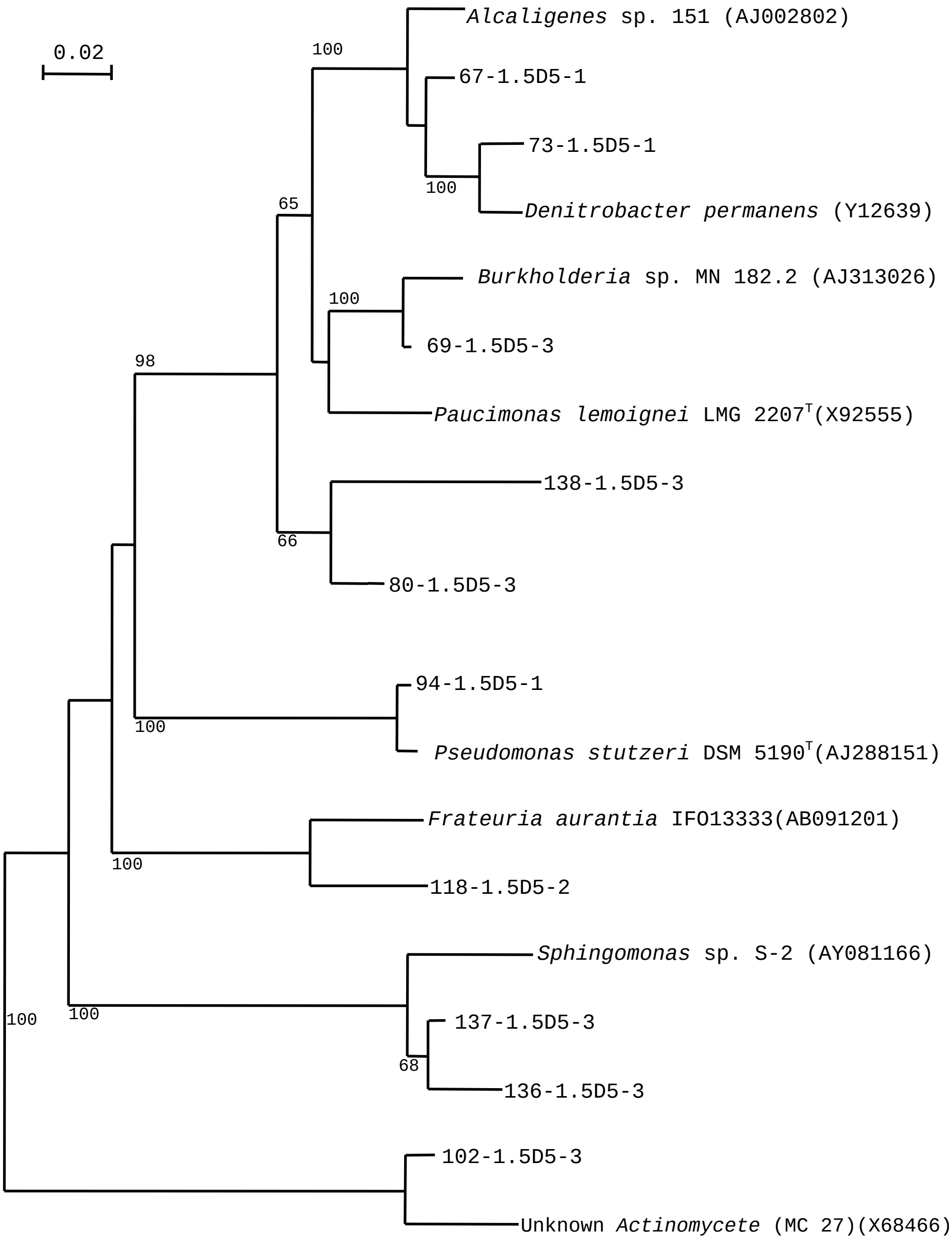

Figure 2B: Neighbour-joining tree showing the phylogenetic positions of cloned PCR amplified a part of the 16S rRNA genes obtained from bio-treatment 1.5DN5 of long-term herbicide contaminated soil, and closed representative 16S rDNA sequences from GenBank. Genbank assession are given and boostrap values are shown at banch points when higher than 60%. Bar, 2 sustitution per 100 nucleotide.

The PCR-SSCP result of microbial community profile in treated samples at three deferent collections is shown in figure 2A. Data presenting in figure 2B indicates phylogenetic positions of cloned PCR amplified a part of the 16S rRNA genes obtained from bio-treatment 1.5DN5 of long-term herbicide contaminated soil, and closed representative 16S rDNA sequences from GenBank. Several bacteria such as *Pseudomonas* sp SETDN1, *Sphingomonas* sp.BDN19 and some representatives of genus *Actinomyces* were isolated and characterized. Other isolated microbes from 1.5DN5 biotreatment and 12 other biotreatments will be identified. The examined culturable microorganisms are capable to anaerobically ans aerobically degrade 2,3,7,8-TCDD; 2,4,5-T; 2,4-D, TCP, DCP or PAHs providing microbial resource for augmentation technology by using anaerobic and aerobic bioreactors in further research and appilation.

Degradation rate

After two year treatment with periodic sampling evaluation of the technology effectiveness indicates that the stimulation of indigenous dioxin and other toxicant degraders became one of promising resolution for developing countries in POP reduction. 50-70% total toxicity was removed in all 13 biotreatments.

We analyzed soil sample before and after two year treatment of 1.5DN5 biotreatment. Result of GC/MS analysis indicates that 51% of total toxicity of several hundreds μg TEQ/g was removed after two year .

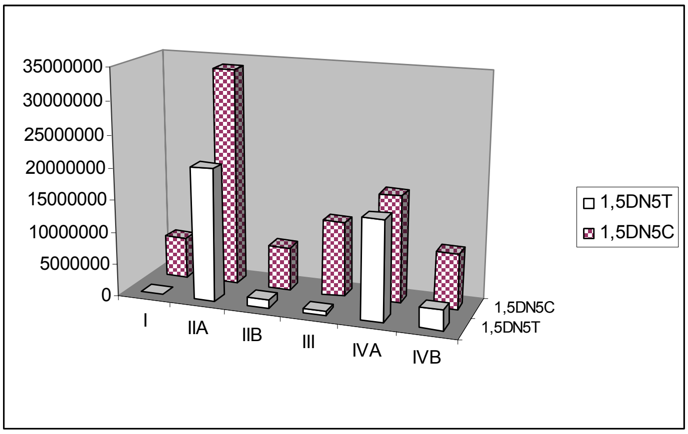

Figure 3: Composition change in soil sample before and after two year treatment

Soil composition change before and after treatment

Table 1

	1,5DN5C (Before treatment)	1,5DN5T (After treatment)
I	2,4,5-T Methyl ester; 2,4-D methyl ester; Acetic acid, (2,4-dichlorophenoxy)	2,4,5-T Methyl ester
IIA	Phenol, 2,4-dichloro-; Phenol, 2,4,5-trichloro-	Phenol, 2,4-dichloro-; Phenol, 2,4,5-trichloro-
IIB	Phenol, 4,5-dichloro-2-methoxy-; Phenol, 2,4,6-trichloro-; Phenol, trichloro-; Phenol, 2,6-bis(1-methylpropyl); Phenol, 2,3,4,6-tetrachloro-; Phenol, 2,3,5,6-tetrachloro-; Phenol, 2,3,5-trichloro-; Phenol, 2,3,6-trichloro-	Phenol, 2,4,6-trichloro-; Phenol, trichloro-; Phenol, 2,6-bis (1,1-dimethylethyl); Phenol, dichloro-; Phenol, 2,6-dichloro-
III	Benzene, 1,2,4-trichloro-3-methoxy; 1,2-Dimethoxy-4,5-dichloro-benzene; Benzene, dichlorodimethoxy- ; Naphthalene, 1,3,7-trichloro-; Benzene, 1,2,4-trichloro-5-ethoxy-	Benzene, dichlorodimethoxy-; Benzene, 1,2,3-trichloro-4-methoxy
IVA	1-Nonadecene; 9-Tricosene, (Z)-; Nonadecane, 2-methyl-; Heptadecane; Tetradecane; Nonadecane; Eicosane; Pentadecane; Octadecane; Hexadecane	1-Octadecene; 1-Nonadecene; Heptadecane;Tetradecane; Nonadecane; Eicosane; Octadecane; Docosane
IVB	9-Octadecenamide, (Z)-; 9-Octadecenoic acid, (E)-; Dodecanoic acid; Dodecanoic acid, 1-methylethyl ester; Octadecanoic acid; n-Hexadecanoic acid; Tetradecanoic acid	9-Octadecenoic acid, (E)-; Dodecanoic acid; Dodecanoic acid, 1-methylethyl ester; Octadecanoic acid; n-Hexadecanoic acid; Tetradecanoic acid; Nonanoic acid; Hexadecanoic acid, methyl ester; Z-7-Hexadecenoic acid

Figure 3 shows composition change in soil sample before treatment in comparison to sample after two year treatment. Not only 2,3,7,8 -TCDD congener was reduced, but also other herbicide contents were decreased too. Comparing chemicals that analyzed in 1.5DN5 sample before treatment and two year treated sample, the change of biodegrading products was detected in treated sample. Some diesel oil compositions were also degraded. This finding shows that bioremediation treatment can be applied for soil with high concentration of 2,3,7,8 -TCDD, 2,4,5-T, 2,4-D, TCP, DCP. Obtained data from GC/MS scanning analysis of the main existing chemicals in soil before and after two year treatment, also shows that bioremediation treatment by 'Active landfill" technology providing promising tool for detoxification of heavily contaminated soils by dioxin and other toxic compounds.

DDT degradation in aerobic bioreactor

Mixture of DDT and other pesticide contaminated soils were collected from "hot spots" in Nghe An province. In these samples, DDT and HCH were found at high concentration, i.e., 175.6 mg/kg and 2282.6 mg/kg, respectively. Besides, other pesticides, including Heptachlor, Aldrin, Dieldrin, Endrin were also detected. In this report, we present obtained results concerning to only DDT degradation by the use of aerobic bioreactor.

For aerobic treatment of POP contaminated soils, bioreactor was conducted for 100kg soil. Bioreactor was designed as a module, it providing an opportunity easier to scale up. The stainless steel bioreactor (Figure 4A) with volume of 100 kg was aerated continuously from the top to the bottom. Water is added frequently through pipes installed from the top.

Fifty kilograms of contaminated soil were subjected into bioreactor, different nutrient substrates, additives, biosurfactant, water etc. were added. Three derivatives of DDT were break down at different rate. DDT at the highest level degraded at the highest rate (Table 2). As usual, DDD was degraded at lower rate. After 30 days, 99.05% three derivatives of DDT removed (Table 2).

Degradation of DDT, DDE and DDD in bioreactor after 30 day treatment

Table 2

Derivatives	**Concentration (mg/kg)**		Degradation rate %)
	Initial sample	After 30 days	
4,4-DDE	4.6	0.025	99.5
4,4-DDD	1.2	0.319	73.4
4,4-DDT	169.8	1.321	99.2
Σ DDT	175.6	1.665	99.05

Application of aerobic bioreactor, DDT was degraded at high rate, i.e., 99.05% in only 30 days. Other pesticides in this sample were almost removed after 30 day treatment. These results will be reported in other papers.

Figure 4A: 100 kg aerobic bioreactor for detoxification of DDT and other pesticide contaminated soils

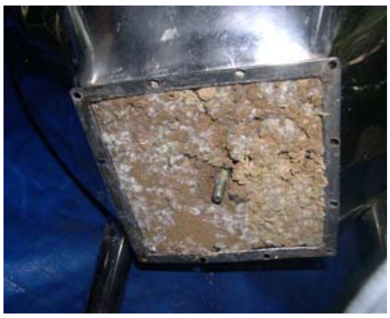

Figure 4B: Soil after 4 day - treatment by aerobic bioreactor

Conclusion

Application of *in situ* bioremediation as well as *ex situ* augmentation treatments not only dioxin was reduced but other contaminated components in soils as 2,4-D; 2,4,5-T, TCP,DCP, PAHs, DDT, DDE, DDD also transformed or degraded. This biotechnology can be applied for detoxification of heavy herbicide/dioxin and pesticide contaminations in "hot spots". Results of microbial diversity indicate that different microbes play certain role and it changes during bioremediation treatments.

Obtained results driving us to develop further research for enhancing POP bioremediation in Vietnam and this technology can be applied for other developing countries.

Part of this results already presented in "Dioxin 2005" in Toronto, Canada

Acknowledgments

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References:

1. Dang T. C.H., Nguyen B.H., Nguyen V.M., Do, Q.H., Pham H.L., Dang V.M. 21th International Symposium on Halogenated Environmental Organic Pollutants and POPs, 2001. Korea. Vol 54: 259-261.
2. Dang T.C.H., Nguyen B.H., Pham T.Q.V., Nguyen T.D., Nguyen Q.V., Nguyen D.N., La T.P., Tran N. H., Mai A.T., Pham H.L., Nguyen V.M., Le V.H., Do Q.H., Dang V.M. 22th International Symposium on Halogenated Environmental Organic Pollutants and POPs, 2002. Spain. Vol.56: 433-436.
3. Dang T.C.H., Nguyen B.H., Nguyen T.D., Mai A.T., Nguyen D.N., La T.P., Nghiem N.M., Nguyen Q.V., Nguyen T.T., Hoang T.M.H., Pham H.L., Nguyen V.M., Le V.H., Do Q.H., Dang V.M. Nov- 2003. Hanoi, Vietnam. Vietnam-US Scientific Workshop: Dioxin screening remediation methodologies, and site characterization: 104-112.
4. Dang T.C.H., Mai A.T., Nguyen Q.V., Trinh K.S., Papke O., Nguyen T.S. 24th International Symposium on Halogenated Environmental Organic Pollutants and POPs. 2004, Germany. Vol 66: 3695- 3701.
5. Dang Thi Cam Ha, Nguyen Ba Huu, Mai Anh Tuan , Nghiem Xuan Truong, Nghiem Ngoc Minh, and Dang Vu Minh. Detoxification of dioxins and other contaminants in soil by bioremediation treatment. Symposium on Halo-ge-nated Environmental Organic Pollutants and POPs. 2005, Canada.

TECHNOLOGY FOR CLEANING UP THE SOILS POLLUTED WITH PCBs, IN THE SERPUKHOV AREA

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The interactions between the amino acid salts and PCBs absorbed in soil were explored, and the structure of transformation products was investigated. The results allowed a method of chemical destruction of C-Cl links and a technology for remediation of soils polluted with PCBs. In full-scale experiments a potential for destruction of PCBs by amino acid salts was demonstrated. Research has to be continued on determining the appropriate doses of the reagent for soils heavily polluted with PCBs.

Keywords: Destruction in situ, amino acid reactant, high levels of pollution with PCBs.

Introduction

The polychlorinated biphenyls are a priority pollutant in the Serpukhov region because over the last 25 years they were used as a dielectric agent by a local industrial plant. This resulted in the heavy pollution of the local environment. The PCBs were taken out of production cycle at the end of the 1980s. However, due to their persistence in the environment and the quantities accumulated in the soils, these chemicals still represent a danger.

The life individual carcinogenic risk posed by the intake of PCBs with food stuffs is estimated at 0.228-1.37 (in the southwest part of Serpukhov) and attains 1.29-7.71 in "Zaborya" region. It must be stated that a risk level of 10^{-3} is already considered a high risk requiring special measures for diminishing it meaning that all inhabitants of Serpukhov live in a highly risky environment.

The studies on soil pollution with PCBs undertaken over the past 18 years showed that the most polluted sites are located in the catchment area of the Borovlyanka stream which is a receiver of the industrial wastewater from the plant. The investigations carried out in 2005 revealed the particularly high contamination of soil and plant samples with PCBs in that region. At one site, the PCB contents in soil was 65342 mkg/kg, that is 1089 times the maximum allowable concentration (MAC). At an other site, the level of pollution was even higher - 340017 mkg/kg (5667 MAC).

The usual options in hazardous waste disposal are thermal destruction and landfilling, but their use is limited by high costs, the need of large areas, etc. The method of microbiological destruction of organochlorinated chemicals has good perspectives but its application is hampered by lack of reliable information on PCB transformation products; so far, this method was most applicable to moderately polluted soils. Therefore, searching for new effective ways of decontamination of soils polluted with organochlorinated products remains a research issue. One promising direction is combining chemical and biological decontamination methods.

Materials and methods

Organochlorinated compounds are capable to react with primary and secondary amines derivates, including amino acids. In this connection we developed a method of PCBs destruction in soils using amino acid based reactants. An alkaline hydrolysate obtained from wastewater coming from tanning industry was used as a source of amino acids; the basic components were sodium salts of amino acids (NaL).

The destruction of PCBs by the amino acid reactant was investigated in topsoil samples taken from transect situated on top, on slope and in the low part of a hill from the Borovlyanka catchment. The soil was loamy and had a slightly alkaline reaction.

Several methods were used to study the destruction of PCBs in the soil matrix: the FTIP method for identification of structural changes in PCB molecules; the gas-liquid chromatography for the total contents of PCBs; and low-resolution and high-resolution mass spectrometry for PCB congeners.

Samples of 200 g bone-dry weight were treated with different doses of NaL. The treatment period was 10 days.

Results and discussion

The contents of PCBs in soil samples has decreased several times after treatment with NaL (Table 1).

Contents of PCBs in soil samples treated with NaL (mkg/kg)

Table 1

Sample	Initial concentration of PCBs, mkg/kg	Concentration of PCBs after treatment with NaL (85 ml/kg)	Concentration of PCBs after treatment with NaL (170 ml/kg)
1	90.6	21.7	21.5
2	117.1	27.2	21.4
3	340016	13292	5403

The treatment with NaL (85 ml/kg) has decreased the content of PCBs in soil from fourfold to 25-fold, as compared to the reference sample. The treatment with a double dose of NaL brought in similar results. In other words, the quantity of PCBs, which was not affected by the treatment, remained approximately the same under both doses of NaL. This can speak for the residual quantity of PCBs being strongly linked to either mineral or humic parts of the soil. Since the humus contents of investigated soils differ it can be assumed that there is sorption of a certain amount of PCBs by the mineral fraction, and that amount is not susceptible to chemical destruction at a single treatment.

The FTIP method was used to establish the mechanism of chemical destruction of PCBs by the amino acid reactants. The analysis of spectra brought us to the assumption that there were interactions between PCBs and NaL, as a result of which the atoms of chlorine in PCBs were partly or totally substituted by radicals -NH-CHR-COONa. The structure of products corresponds to the formula:

$$C_{12}H_{10\text{-}n}Cl_{n\text{-}m}(NH\text{-}CHR\text{-}COO)_m + NaCl_m,$$

where *n* is the number of atoms of chlorine in the initial PCB molecule, and *m* is the number of -NH-CHR-COO radicals in the product.

The spectrum of soil washed out with water practically coincides with the spectrum of soil washed with solvents: this suggests that the reaction products are soluble and can be extracted from the particles that have adsorbed the PCBs (Figure 1).

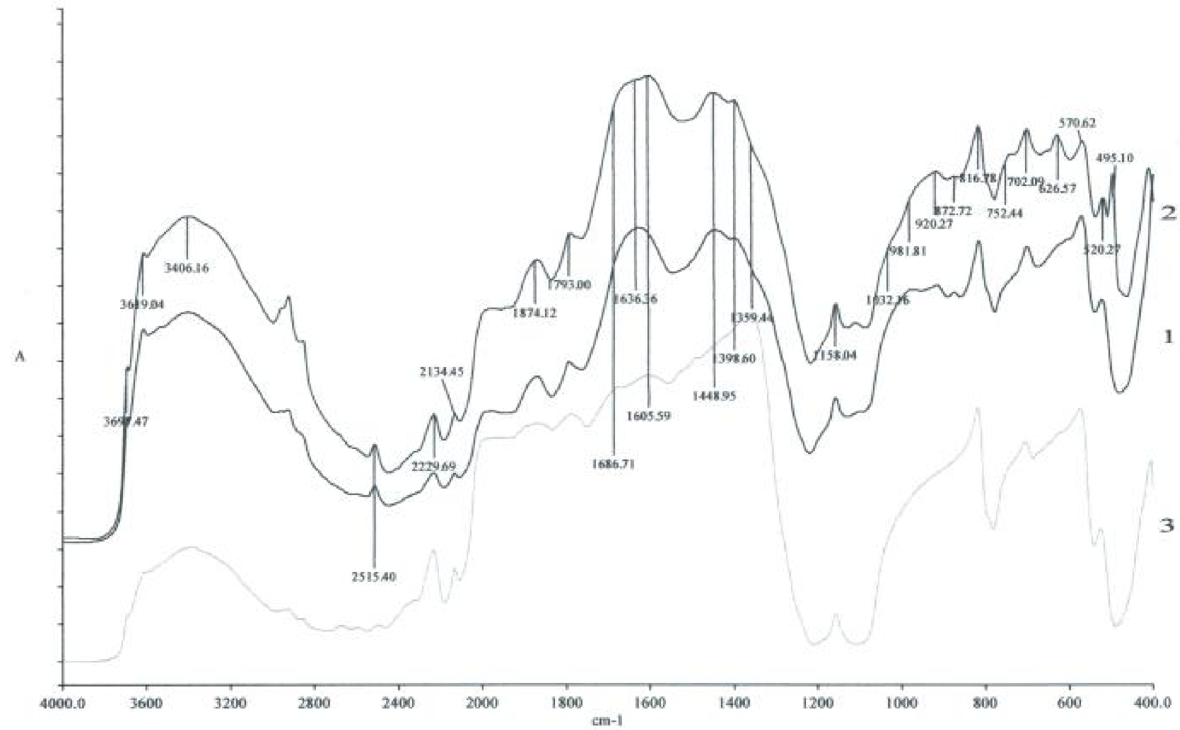
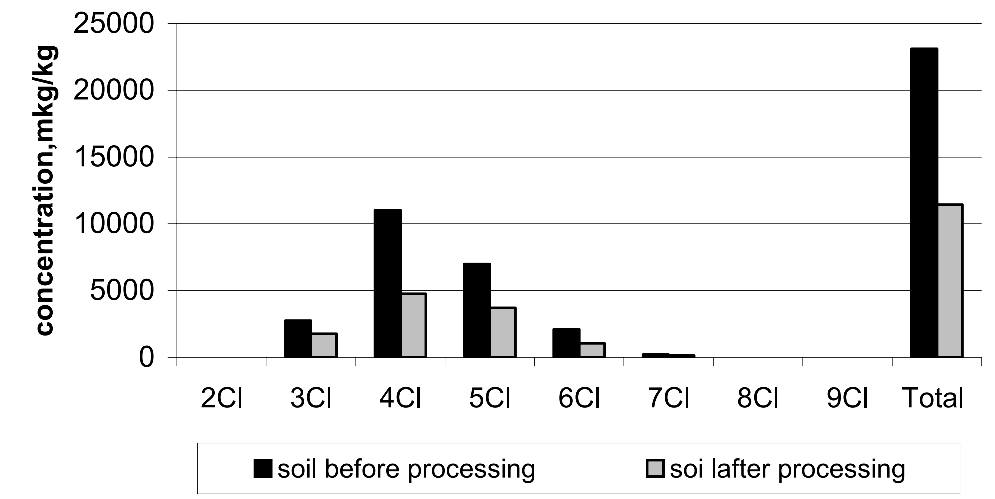


Fig.1 Spectra of soil keeping PCBs (1), soil by an impregnated aminoacidic reactant (2), washed soil (3)

The next stage of the experiments on PCBs destruction was conducted *in* situ, at a heavily contaminated site in the Borovlyanka catchment. Experimental parcels, 0,25 m^2 each, were used for the study. The parcels were laterally isolated by 20 cm deep casing.

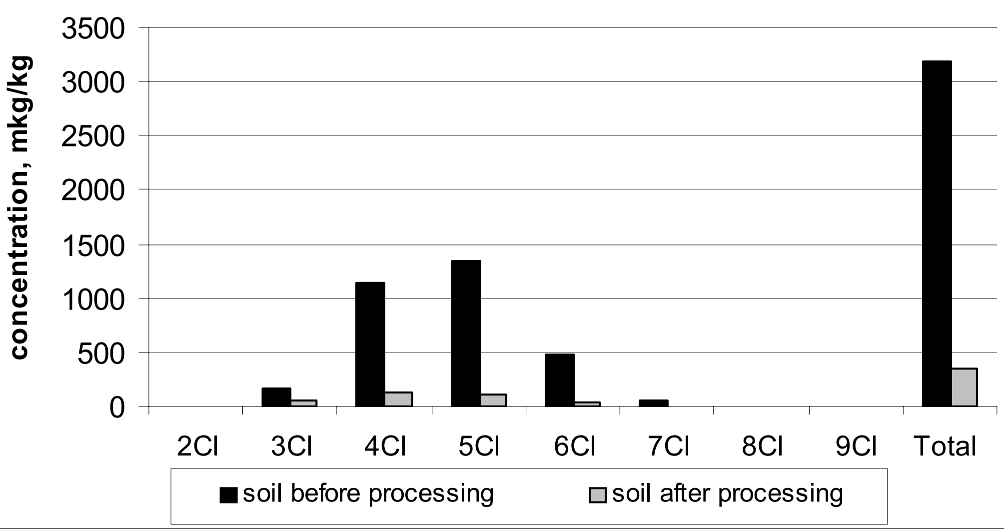
The soils treated by a minimum dose of reactant, the contents of PCBs has decreased approximately threefold; the ratio of congener groups has changed insignificantly, the sum of light fractions is 50.5% (Figure 2).

Fig.2 Concentration PCBs before processing by an aminoacidic reactant №1

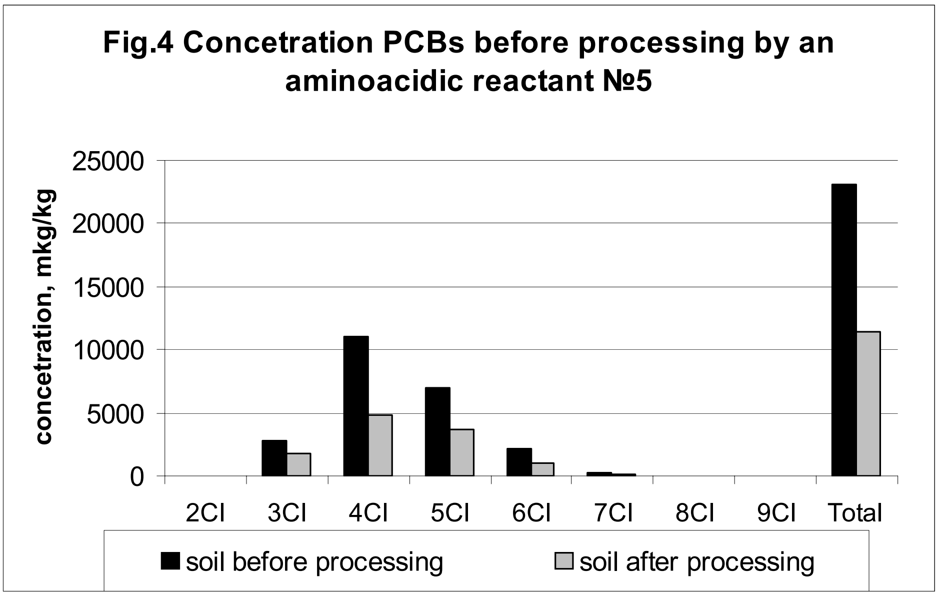


The treatment of the least contaminated soil (parcel 4) brought in the most spectacular decrease of the contamination level: the PCB concentration has decreased –more than ninefold. The contents of light fractions increased up to 53 % (Figure 3).

Fig.3 Concetration PCBs before processing by an aminoacidic reactant №4



The treatment of soils with higher degree of contamination (parcel 5), with small doses of reactant proved to be the least effective – the contamination level has decreased only twofold (Figure 4).



Conclusion

1. Under laboratory conditions, a PCB detoxification effect in soil samples was obtained showing a significant reduction of the level of persistent organic compounds.

2. The dose of an amino acid reactant of 85 ml/kg (at 2 mol/l) provides the destruction of all chemically accessible PCB for the given exposure time (10 days).

3. Investigations using the FTIP method have shown that the intensity of C-Cl oscillations in PCB-containing soil treated with an amino acid reactant considerably decreases during several days that mirrors the dynamics of replacement of chlorine atoms for amino acid radicals.

4. The change of the ratio between homologous groups of congeners in the soils gives evidence of interactions between PCBs and amino acid derivates and the gradual replacement of chlorine ions by amino acid radicals.

5. Generally, it can be stated that good results were achieved in experiments on destruction of PCBs in soils by treating them with salts of amino acids. However, it is necessary to carry on the experimental studies, specifically for soils heavily contaminated with PCBs.

Section V

Remediation of pesticides contaminated sites

ASSESSMENT OF PESTICIDE POLLUTION IN FRAME OF OLD PESTICIDE STORAGE AND SURROUNDING TERRITORY (Balceana case study).

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The objective of this study was an assessment of the pesticide pollution level in soil in frame of old pesticide storage near Balceana village and surrounding agriculture territory. The concentration of obsolete pesticides was compared with other four sites from Hincesti region of Moldova. GC and GC/MS techniques were used with appropriate sample preparation technology. The large range of the pesticide concentration was determined in soil samples from investigated sites: HCHs 1,0 – 24700,0 μg/kg; DDTs 8,0 – 365600,0 μg/kg. The spatial analysis showed a strong pollution impact to surrounding agriculture territory near Balceana old pesticide storage. The distance from 100 to 500 m form site boundary is characterized by high pollution level of DDTs (more that 3 times higher that MAL for soil). The high HCHs concentration is determined only in frame old pesticide storage. Were determined that principal ways of the pesticide fate into the environment is dispersion by wind with dust soil material. The anomaly with the high DDTs concentration is explained by the insufficient management by the utilization of this chemical in the past. Borehole showed a principal DDTs pollution to the depth near 1 m which do not reach ground water level. The investigated territory needs a control of the agriculture production and other land use.

Key words: DDTs, HCHs, Gas Chromatography, soil pollution, pesticide fate, site assessment, MAL.

Introduction

Persistent Organic Pollutants (POPs) are synthetic chemical substances with unique and harmful characteristics. They are highly toxic to wildlife and humans and have become common contaminants in fish, dairy products, and other foods around the world. They include some of the world's most harmful chemicals including highly toxic pesticides such as HCH, DDT; industrial chemicals such as PCBs; and unintended by-products of industrial processes and incineration such as dioxins and furans. The management of domestic and hazardous wastes is considered as one of the most urgent environmental problems in Moldova. Currently in Moldova approximately 3000 tones of obsolete pesticides are stored in various former collective agricultural warehouses or disposed in uncontrolled dumps [1]. However the information about the actual status of obsolete pesticides after the repacking on former storages is not sufficient at present. This investigation is important also for the assessment what remediation technologies can be used for the future soil detoxication.

The aim of this study was an assessment of the pesticide pollution level in soil in the frame of the storage near Balceana village and surrounding agriculture territory after the repacking of old pesticides. The following objectives were realized for this goal:

- determination of pesticides concentration in top soil layer;
- assessment of spatial pesticide distribution in top soil on neighbor territory;
- comparison of the pollution level from other pesticide storages.

Materials and methods

Site selection

Five sites were previously investigated for the assessment of different site condition in Hincesti region of Moldova. Every site was characterized at least by tree soil samples. The site with the high pesticide level and appropriate landscape without natural or artificial barriers was chosen for the more detail investigation.

Sampling

Soil sampling was made by regular basis in the frame of polluted site and by four intersections in different direction from site. Two intervals 0 - 20 and 20 – 40 cm were used for the soil sampling in the frame of pollution site. The intersections were sampled from the soil depth 0 - 20 cm on the different interval from polluted sites. The distance of the soil sampling from polluted site was from 275 to 500 m. Boreholes were sampled in the interval 30 – 50 cm to the ground water level.

Analytic determination

Gas Chromatography with μECD is the best sensitivity method for organochlorine compounds determination in different media [2-5], which was used in present study. EPA method with the appropriate sample preparation techniques was used for pesticide determination. The soil samples were extracted in two repetitions. All reagents:solvents, standard solutions of HCHs (□□□□, DDTs (4,4-DDE, -DDD, -DDT), anhydrous sodium sulphate, silica gel, pure gases were of the pesticide grade purchased from Supelco-Aldrich, Agilent Technologies, Linda Gas etc. The method parameters are presented in the table 1.

Experimental Conditions

Table 1

System elements	Method parameters
Injection ports:	Split/splitless inlet; injection – Split 5:1, 2 µl, inlet temperature of 300°C,
Column	HP5 - 30 m Length, 320 µm I.D., 0,25 µm Film.
Carrier gas	H_2, 1,5 ml min^{-1}, or Average Velocity 30 cm sec^{-1}, Constant Flow
Oven	First ramp: 100°C (hold 1 min) to 200°C at 20°C min^{-1} hold time 3 min Second ramp: 200°C to 280°C at 10°C/min hold time 3 min (Total time 20 min)
Detector	63Ni µECD, 320^0 C, N_2 makeup, 60 ml min^{-1}
Data collection	ChemStation

Spatial analysis

The local coordinate system was used for the sample point affixment (Moldref system). This approach gave us the possibility to use GIS software ArcView 3.2a. The interpolation of the pesticide concentration in soil was made by Kringing method developed in this software. The correction of pesticides spatial distribution for the territory out of the site was made by taking into consideration natural and artificial landscape barriers. Moldavian normative indicates Maximal Admissible Level (MAL) of 100 □g/kg for pesticides in soil (sum of HCHs or DDTs). We analyzed areas with the HCHs and DDTs concentration higher of this MAL.

Results and discussion

The middle pesticide concentration in top soil of five investigated sites is presented on figure 1. The biggest value is indicated on Bujor site where middle HCHs concentration is 17333 □g/kg (min <0,1; max – 24703 □g/kg) and DDTs concentration 124415 □g/kg (min - 3412; max – 365549 □g/kg). The level of 50000 □g/kg is maximal limit after that any soil is determined as a toxic waste. This territory needs an action for the inventory and removal of this toxic waste. Balceana storage has a high level of pesticide pollution and was selected as place for the more detail investigation. This territory can be meliorated by the environmental friendly technology like phytoremediation etc. Other investigated sites showed relative low concentration in frame of old storage territory.

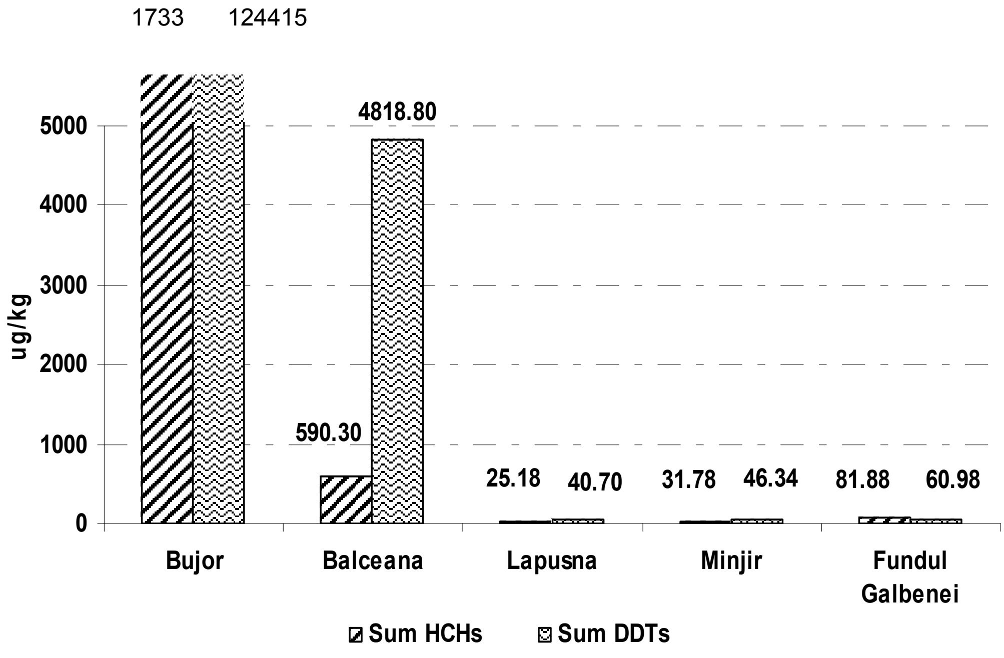


Figure 1. Pesticide concentration in top soil from old pesticide storage: middle value, □g/kg.

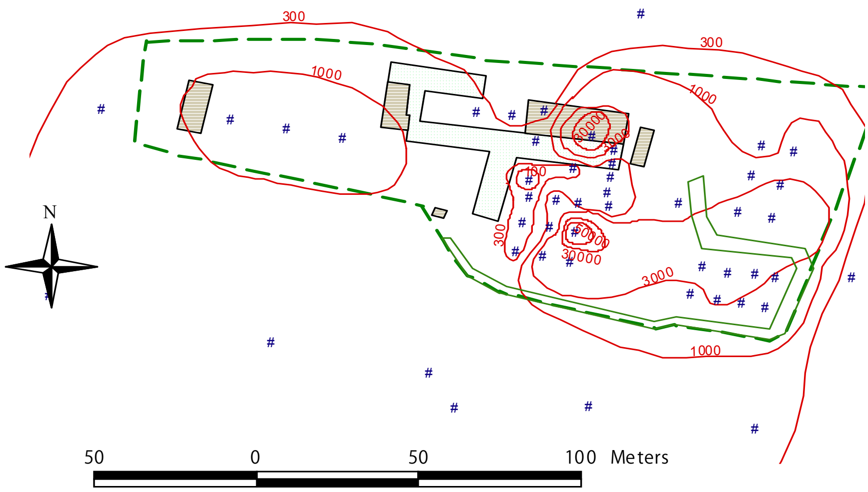


Figure 2. Sampling plan and DDTs pollution of Balceana old pesticide storage, □g/kg

Balceana site and surrounding territory was studied more detail. 90 soil samples were taken on the site and surrounding territory. The more important problem for this site is DDTs pollution with the large interval of concentration: from 100 to 64045 µg/kg. The sampling plan and the spatial distribution of DDTs and HCHs are presented on figures 2 and 3. The DDTs and HCHs distribution is logarithmical and contour interval is not linear. The areas of the territory polluted by DDTs and HCHs are presented in table 2. The polluted area o DDTs exceeds HCHs polluted territory in more that 26 times. The total polluted area for DDTs consists of 15,24 hectares. The territory with the DDTs pollution interval of 300 – 1000 µg/kg is a principal (75% of territory). The soil with the area 39,6 m^2 can be determined as toxic waste with the concentration higher that 50000 µg/kg.

The DDTs and HCHs spatial distribution by the investigated area

Table 2

Interval of concentration for DDTs □g/kg	Area, m^2	Area %	Interval of concentration for HCHs □g/kg	Area, m^2	Area %
100 - 300	188.0	9.83	100 - 300	2397.0	41.38
300 - 1000	558.0	75.00	300 - 1000	2513.0	43.39
1000 - 3000	257.2	11.15	1000 - 3000	731.0	12.62
3000 - 10000	168.8	3.19	> 3000	151.0	2.61
10000 - 30000	28.0	0.69			
30000 - 50000	122.8	0.12			
> 50000	39.6	0.03			
Total polluted area	**152434.9**	**100.00**		**5792,0**	**100.00**

The DDTs and HCHs distribution correlates. Two anomalies with the extra high concentration in frame of storage territory are indicated near old founding and on the middle site of the storage. The main flow of the spatial migration of DDTs and HCHs by storm water is oriented from west to east (from higher elevated site to lower). Other way of DDTs fate is a migration by wind. Figure 4 illustrated spatial distribution of DDTs on the surrounding territory.

The additional anomaly with the concentration of 14693 □g/kg is presented at the north-east direction. The region with the concentration interval 300 – 1000 □g/kg is spreading by principal wind direction from north-east to south-west. The landscape also impacts to this pesticide distribution. The pesticide concentration by four intersections is presented on figure 5.

Figure 3. Sampling plan and HCHs concentration in soil from Balceana old pesticide storage

The more polluted areas are situated by the principal wind directions from north-east to south-west. The anomaly of DDTs outside of pesticide storage can be explained by the insufficient management of these pesticides in the time of there utilization. The principal distribution is characterized by the logarithmical trend from points with extra high level of concentration.

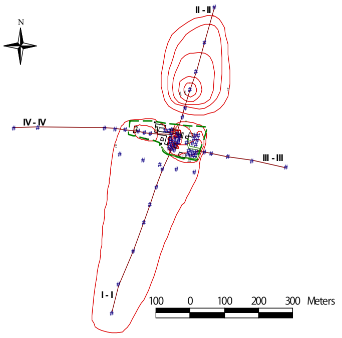
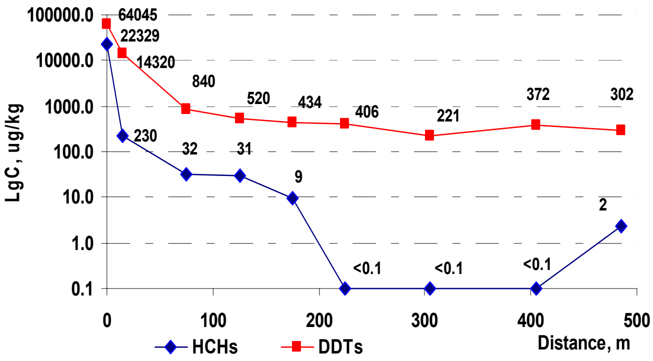


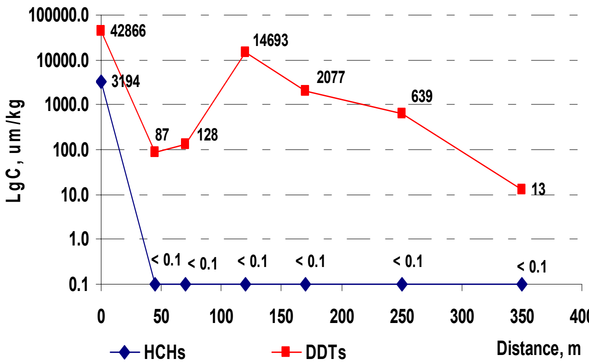
Figure 4. Spatial distribution of DDTs on the surrounding territory where I-I, II-II, III-III, IV-IV are intersections for analysis of pollution impact to the surrounding territory.

The pesticide fate by soil profile is presented on figures 6 and 7. The middle value of HCHs decreases from 1267 for the interval of 0 – 20 cm to 11 □g/kg for the interval of 20 – 40 cm (120 times). The reduction of DDTs concen-tration is from 6614 for the interval 0 – 20 cm to 555 □g/kg for the interval 20 – 40 cm (12 times). The distribution by soil profile in boreholes has logarithmical trend. The depth of principal pollution consists of 1 m. Further fate is absent below of 1 m and we can speak that is not strong ground water pollution on the site.

Intersection I - I



Intersection II - II



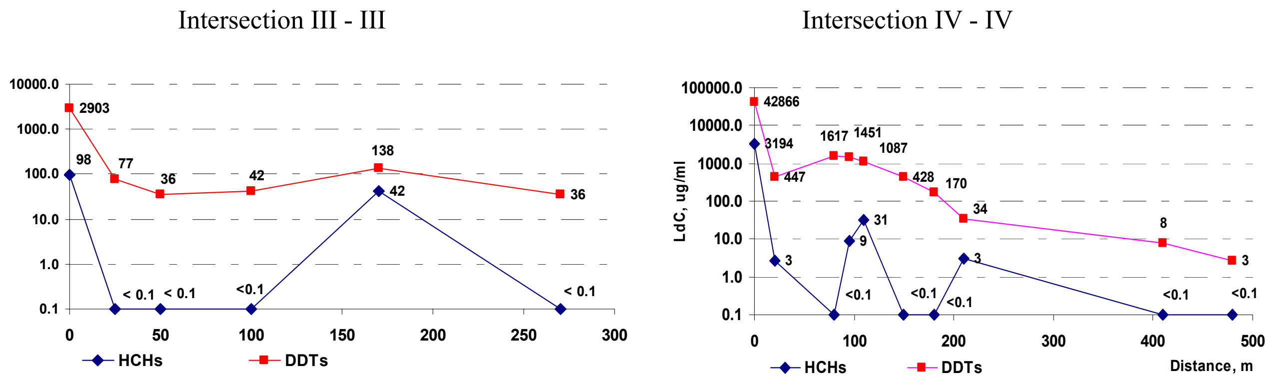


Figure 5. Pesticidesdistribution in soil samples along intersections I–I, II–II, III–III, IV-IV.

Conclusions

The pollution level exceeds MAL on two sites among five assessed storages. So we can speak that extra high pollution level of pesticides is remained in soil after the pesticide repacking on 40% of investigated storages. Balceana pesticide storage was selected for the detail investigation if this territory can be clean by phytoremediation technology. The detailed study showed this territory is polluted strong by chlororganic pesticides. DDTs metabolites have higher pollution level in the comparison with HCHs.

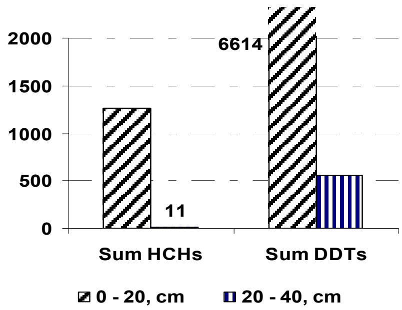


Figure 6. Comparison of DDTs concentration by intervals of 0 – 20 cm and 20 – 40 cm (middle value).

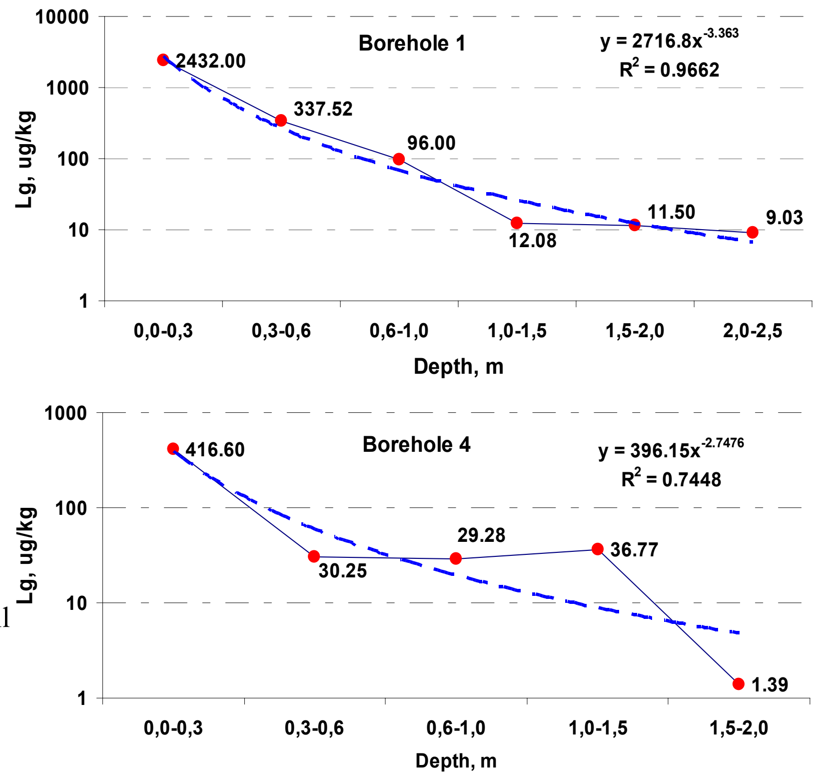


Figure 7. DDTs distribution by soil profiles

The spatial analysis showed a strong pollution impact of DDTs to surrounding territory. The actual utilization of investigated area is agriculture production. The distance from 100 to 500 m from the site is polluted more by the principal wind direction. The fate of DDTs can by explained by the migration with dust soil material. The ground water is not polluted strong that can be explain by soil properties like granulometric composition and big organic content. The anomaly with high pollution level presents near this site as the past pollution event. The high HCHs concentration is determined only in frame old pesticide storage. The investigated territory needs a control of the agriculture production. The other land use is recommended for this polluted site. The remediation of this territory is possible for the improvement environmental quality.

References:

1. National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants. (2004) Ministry of Ecology and Natural Resources, World Bank, Chişinău, Ştiinţa, 80 p.
2. Lourencetti C., Navickiene S., Ribeiro M.L., Santiago-Silva M. (2004) Determination of Organochlorine Pesticides and Polychlorinated Biphenyls Residues in Municipal Solid Waste Compost by Gas Chromatography with Electron-Capture Detection. Chromatografia, 59, pp. 769–773.
3. Martens D., Gfrerer M., Wenzl T., and others (2002). Comparison of different extraction techniques for the determination of polychlorinated organic compounds in sediment. Anal Bioanal Chem 372, pp. 562–568.
4. Pirard C., Focant J.F., Pauw E. (2002) An improved clean-up strategy for simultaneous analysis of polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), and polychlorinated biphenyls (PCB) in fatty food samples Anal Bioanal Chem 372, pp. 373–381.
5. Wolska L. (2002) Miniaturized analytical procedure of determining polycyclic aromatic hydrocarbons and polychlorinated biphenyls in bottom sediments. Journal of Chromatography A, 959 pp. 173–180.
6. Method 8081A: Organochlorine Pesticides by Gas Chromatograph. EPA 1996, 44 p.

REPUBLIC OF BASHKORTOSTAN, RUSSIA: INVENTORY OF OBSOLETE PESTICIDES AND INVESTIGATION OF A MEGA-SITE CONTAMINATED BY PCDD/Fs

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For 10 years monitoring of dioxin pollution has been carried out what permitted to reveal a mega-site of extreme dioxin pollution connected with production of phenoxyherbicides in Ufa, Russia. Though the plant was closed in 2004 no decision on methods of pollution elimination was taken. The problem is utilization of 500,000 tons of PCDD/Fs polluted sludge, cleaning and rehabilitation of more than 100 hectares of the plant territory to the depth of 2 and more meters and the equal area directly adjoining the plant, destruction and burial of about 100 production shops and buildings.

32 thousand tons of pesticides have been used in the Republic of Bashkortostan (1990-2000), the major part of them are herbicides - over 25 thousand tons. About half of the total amount of herbicides (over 10 thousand tons) makes 2.4-D amine salt. The volume of pesticides with expired term of storage and forbidden for use in the Republic of Bashkortostan is about 250 tons.

Key-word: phenoxyherbicide, dioxin, polluted zone, 2,4-D, obsolete pesticides.

For creation of a National Plan of Actions on realization of the Stockholm Convention in Russia the assessment of true situation with POPs pollution in separate regions of the country is especially important. The Republic of Bashkortostan situated in the South Ural is a part of the Privolzhsky Federal Okrug and is most investigated in terms of dioxin pollution.

In 1994-2000 a republican program “Dioxin” was carried out. In the course of its realization the inventory of dioxin pollution in the region was made, PCDD/Fs and PCBs-WHO background levels were stated in the environment, biota, human biological tissues (blood, adipose, breast milk and placenta) and food stuff. The causes and sources of dioxin pollution were revealed.

It was stated that the Republic of Bashkortostan is a region with considerable dioxin load on environmental objects, living nature and population as a result of phenoxyherbicide production. If PCDD/Fs pollution of the total area of the republic is estimated as inconsiderable (what is confirmed by the background pollution level of living organisms inhabiting soil and water, meat and milk of cattle, human blood and breast milk), pollution of industrial centers is evaluated as middle or low, then the territory of the JSC “Khimprom” was and still remains the area of high pollution and risk for man (Fig. 1-3).

It was determined that “dioxin trace” is coming out from the epicenter – the territory of the chemical plant, PCDD/Fs are spreading with dust and carried by motor transport. The results of pollution are expressed in increased PCDD/Fs level in human blood and breast milk of the population, 2.3.7.8-TCDD pollution is prevailing. At the background level and in buffer zones PCDD/Fs pollution of living organisms is taking place with the effect of bioaccumulation from 6 to 15, depending on peculiarities of vital functions of animals and presence of adipose component of tissue.

In impact zones disequilibrium in the system “a biological object – the environment” is taking place due to extremely high pollution comparable with lethal dozes at acute poisoning. It is advisable to carry out biomonitoring of dioxin pollution by using living organisms with relatively long period of life. This requirement is met by human biotissues in which PCDD/Fs bioaccumulation is by 20 times higher than for other mammal. Analysis of distribution of PCDD/Fs concentration in blood and breast milk of the population in the region made it possible to perform ecological and geographical zoning of the territory, to reveal the results of PCDD/Fs transboundary transport.

As source data for making models of dioxin pollution the results of PCDD/Fs determination in environmental objects, biota and human biological tissues grouped by 3 scenarios were used: I – conditionally clean zone (rural areas of RB), II – urban areas (Ufa as an example), III – extreme pollution zone (“Khimprom”) (Figs 1-3).

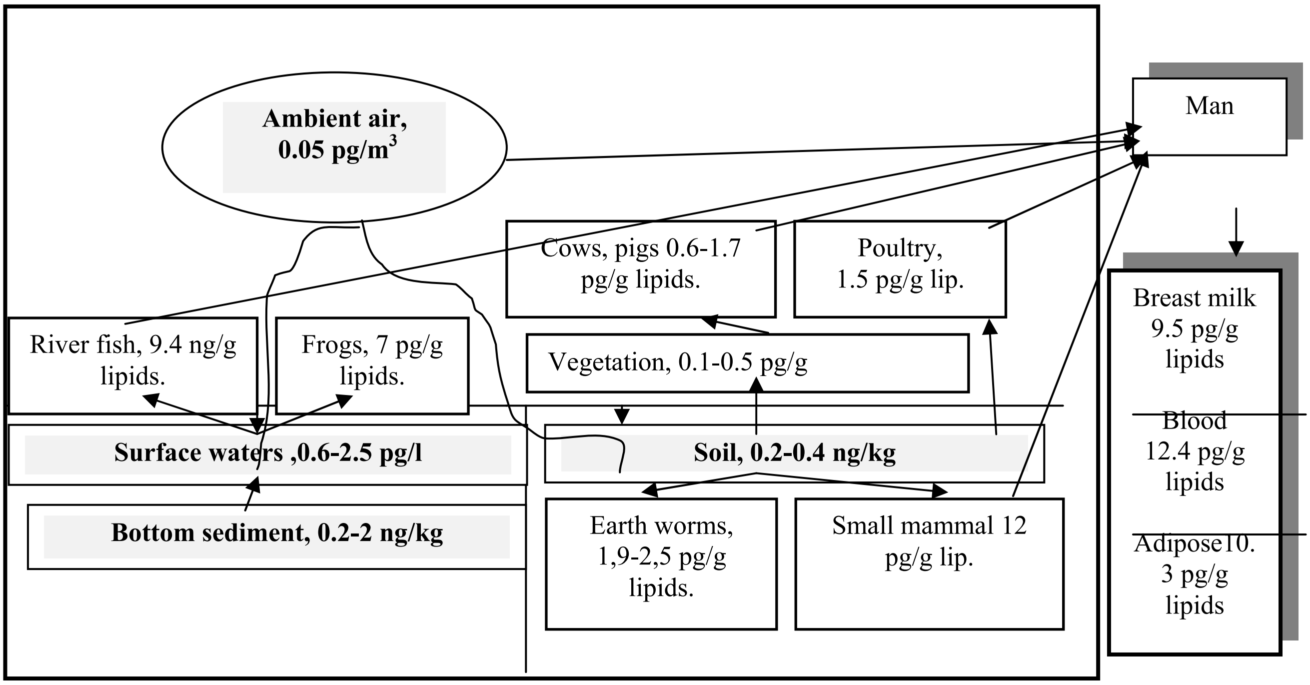

Figure 1. Scenario I. Background pollution of rural areas of Bashkortostan.

In scenarios I and II mean values of PCDD/Fs content in municipal sewage water, mean data on PCDD/Fs content in breast milk, blood and adipose tissue of population in some rural and urban areas of the region were used.

For description of the impact zone the data of analyses of soil, sludge and production were used. Data on PCDD/Fs concentration in blood were also used. The maximum value corresponds to the data for workers of chlororganic production, the minimum value – to the background level of "Khimprom".

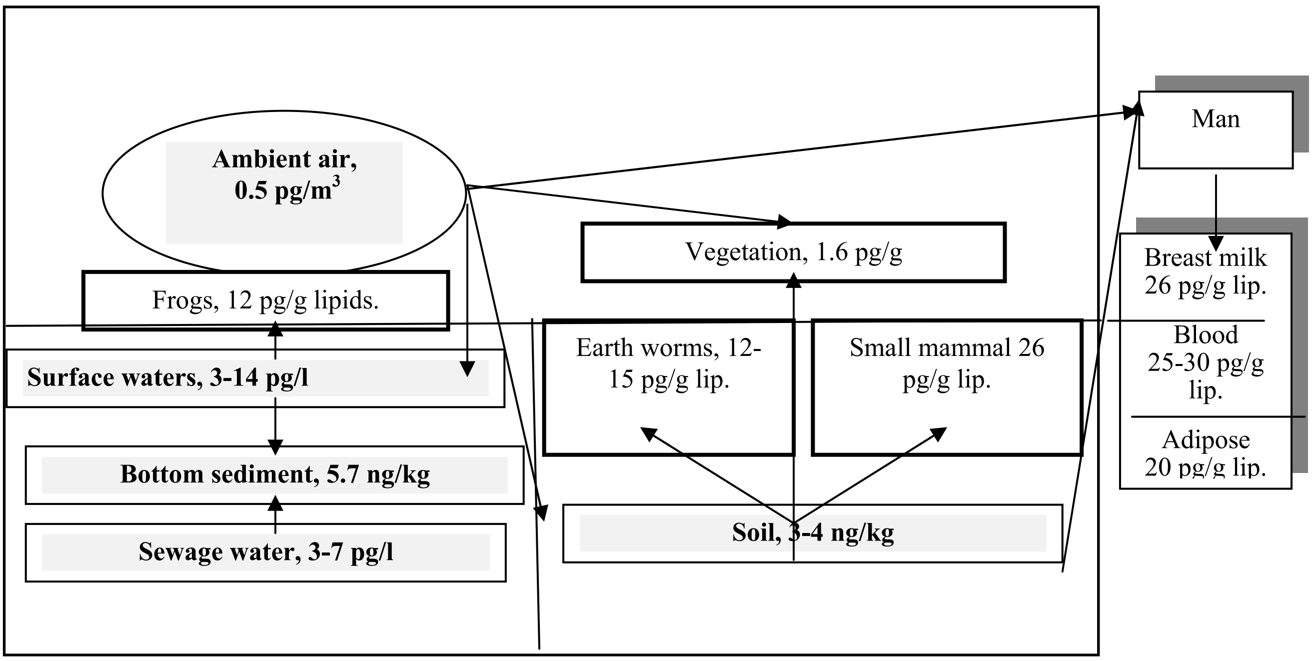

Figure 2. Scenario II. Urban areas of Bashkortostan.

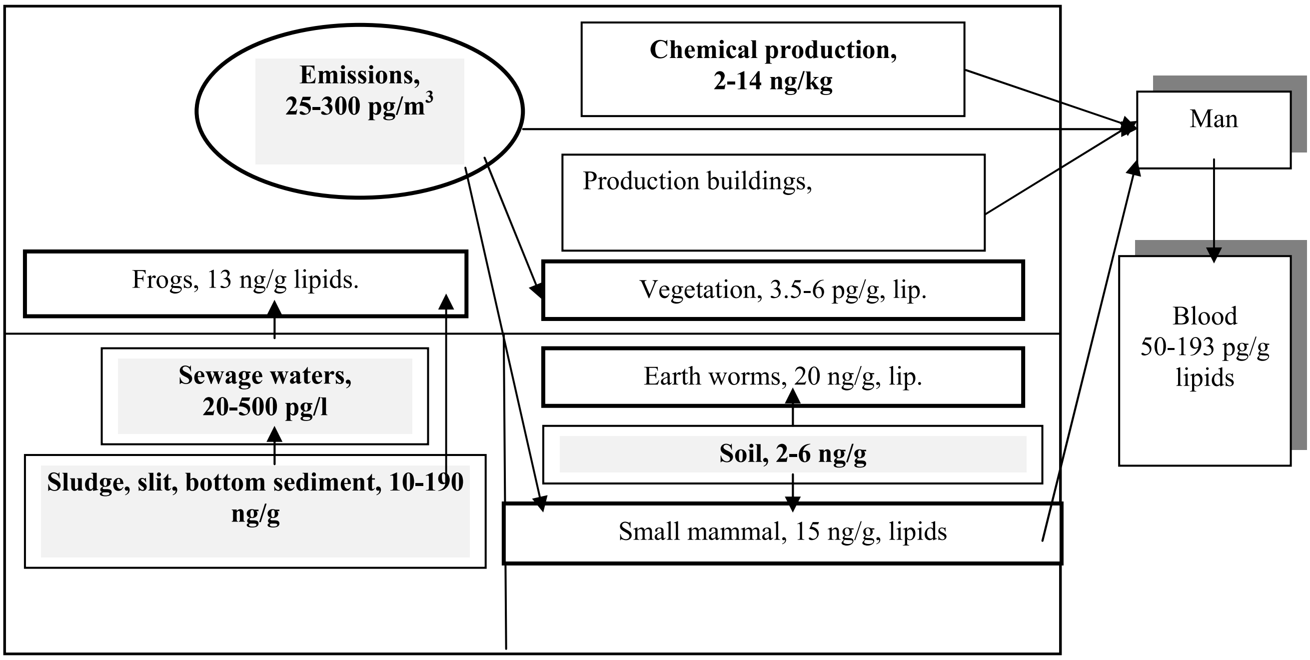

Figure 3. Scenario III. Industrial pollution zone, Ufa, chemical plant.

Scenario of the chemical plant territory pollution during the period of 2,4,5-T and 2,4,5-TCP production (the 60s-70s) (Fig.4) was constructed by means of extrapolation of data on PCDD/Fs content in environmental objects and human tissues assuming that PCDD/Fs half-life in soil is 10 years, in sludge and slit – 15 years, in human biotissues – 7.4 years.

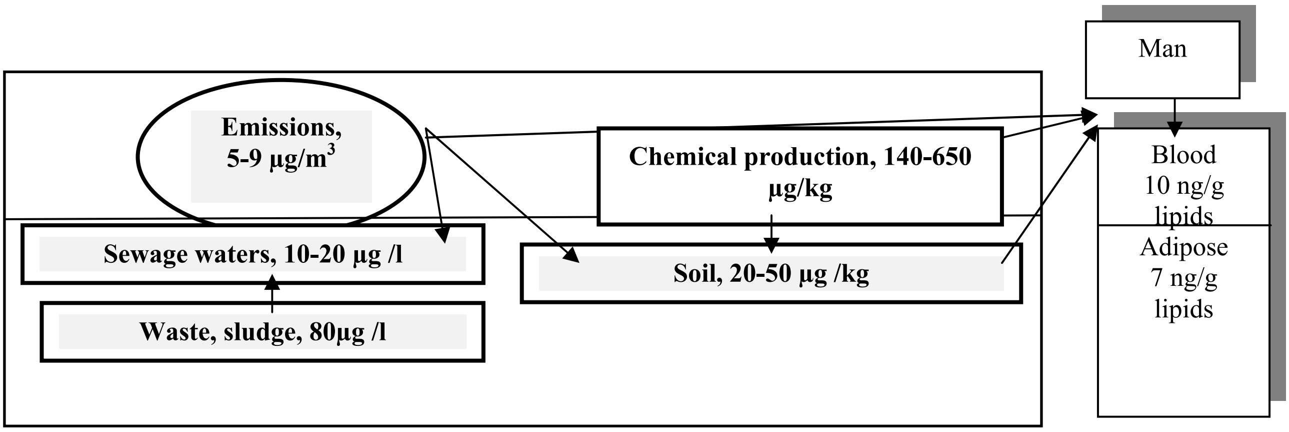

Figure 4. Scenario IV. Zone of extreme pollution, the territory of "Khimprom", the 60s-80s (retrospective, calculation)

The forecast for development of ecological situation in the region is determined by the presence of a pollution source and slowed processes of PCDD/Fs isomer destruction.

If no measures on rehabilitation or conservation of the territory are taken then PCDD/Fs transfer from impact zones, dilution and gradual accumulation in urban areas is inevitable.

Soil in rural areas and river network of the region have a sufficient potential for preserving low PCDD/Fs levels, the current entry is inconsiderable and so far does not affect the levels of biota pollution in background regions.

A more complicated situation may arise in terms of exposure of the population in the region. Study of toxicokinetics mechanism of PCDD/Fs accumulation shows that due to relatively long life even a small increase of PCDD/Fs entry may result in their considerable accumulation in human tissues and excess of allowable concentration recommended by the WHO.

Monitoring of dioxin pollution has been carried out for 10 years. That permitted to reveal a zone of extreme pollution (up to 200 ppb TEQ PCDD/Fs) connected with production of phenoxyherbicides in Ufa [1]. The mega-site of dioxin pollution covers over 134 km^2 (1/3 of the city area) with the population of more than 250 thousand people what by many times exceeds the scale of the incident in Sevezo, Italy [2]. The number of PCDD/Fs exposed workers (the mean level of 550 pg/g blood lipids) is over 3000 people, the population of the city (more than 1.2 million) has the increased PCDD/Fs background level in breast milk, blood and fat by 30-50% exceeding the average European level [3].

Comparison of Ufa incident with explosion in Seveso

Table 2

Parameter	**Seveso** [5]	**Ufa** [4]
Incident type	Explosion of reactor	Production, emergency emission
Period of operation	1970-1972, 1975-1976 (TCP, 150 ton/year)	1965-1967 (2,4,5-T, 100 ton/year) 1962-1987 (TCP, 1000 ton/year)
Incident time	1976	1962-1987
The area of the impact	Zone A – 0.8 km^2 Zone B – 2.7 km^2 Zone R – 14.3 km^2	Zone F – Khimprom – 1.4 km^2 Zone G – industrial zone – 5 km^2 Zone H – district of Ufa – 134 km^2
Soil pollution level, 2378-TCDD	Zone A – 2.3 – 54 ppb Zone B – 0.01 – 0.4 ppb Zone R – 100 ppt	Zone F – 10-200 ppb Zone G – 0.01 – 0.2 ppb Zone H – 3-9 ppt
Human impact	187 cases of chloracne	More than 135 cases of chloracne
Number of exposed people	Zone A - 736 Zone B – 4,737 Zone R- -31,800 Non-ABR-185,225	Zone F - >3,000 (workers) Zone G – 2,500 Zone H - >300,000 Non-FGH-800,000
2378-TCDD in blood samples, ppt, lipids based, mean or interval	Zone A - 828–56,000 (n=19, 1976), 61.5 (n=6, 1992/3), 16.6-262.1 (n=33, 1993/1998) Zone B – 16.8 (n=52, 1992/3), 7.0-95.0 (n=36, 1993/1998) Zone R-0.5-18.4 (n=73, 1993/1998) Non ABR–5.3 (n=52, 1992/3)	Zone F – 267 (n=39, 1992), 125.1 (n=38, 1995/7), 548.9, max 4101.2 (n=32, 1998/01) - workers Zone G – 26.6 (n=5, 2004) Zone H – 15.9 (n=23, 1998-2004) Non FGH–12.1 (n=35, 1998/2005)
Utilized materials	Tank Seveso – 200,000 m^3 Tank Meda – 80,000 m^3	530,000 m^3 of sludge, (>11.2 ppb) 46,200 m^3 of soil, (>10ppb), 50,000 m^3 of toxic waste (up to 200 ppb) >500,000 m^3 of buildings (<15 ppb)*

*this value may be by an order higher because not all buildings have yet been examined.

The source of pollution for 60 years had been a chemical plant Khimprom releasing chlorophenol and phenoxyherbicide production until 1987. Though the plant was closed in 2004 no decision on methods of pollution elimination was taken[4].

The problem is utilization of 500,000 tons of PCDD/Fs polluted sludge (from 20 up to 200 ppb), cleaning and rehabilitation of more than 100 hectares of the plant territory (the ground polluted to 15 ppb to the depth of 2 and more meters) and the equal area directly adjoining the plant (0.2 – 1 ppb), destruction and burial of about 100 production shops and buildings the plaster of which is polluted to 20 ppb.

According to official statistics at present the volume of pesticides with expired term of storage and forbidden for use in the Republic of Bashkortostan is about 250 tons including over 6 tons of granosan and about 8 tons of biological preparations that are to be utilized/buried.

For the period of 1990-2000 ys.32 thousand tons of pesticides have been used in the Republic of Bashkortostan, the major part of which are herbicides - over 25 thousand tons. About half of the total amount of herbicides (over 10 thousand tons) makes 2.4-D amine salt that has been produced in Ufa for 50 years. The list of applied pesticides is large and includes over 150 names of preparations: acaricides, disinfectants of seed, fungicides, herbicides, desiccants, biopreparations.

The problem of utilization of relatively small amounts of pesticides with expired term of storage and forbidden for use is complicated by their storage in different places and the absence of plants for utilization.

There is one more problem connected with pollution of the territory of the Institute of chemicals for plant protection also situated in Ufa. It was here that for many years formulae of phenoxyherbicide production had been developed, production of pilot batches and testing of new herbicides had been carried out.

Residual pollution of the Institute territory by chlororganic compounds including PCDD/Fs is rather large (dioxin pollution level of 4ppb and more has been revealed in the place of former greenhouses that are now destroyed). The position of this local source of pollution by chlororganic pesticides, products of decay and dioxins practically within the city boundaries is really hazardous for population. Local pollution sources of this kind – hot spots of dioxin pollution also demand the development of methods for rehabilitation of polluted objects, cleaning of production buildings, decontamination of soil or its burial.

References:

1. Amirova Z, Amerkhanov K, Kruglov E, Lozhkina E, Khalilov R. *Organohalogen Comp*, 1999; 44;299.
2. Amirova Z, Kruglov E. *Organohalogen Comp*, 2005; 67, 2094.
3. Amirova Z, Kruglov E, Loshkina E, Khalilov R and Khalikova N. *Organohalogen Comp*, 2005; 67,1684.
4. Amirova Z, Kruglov E, Maystrenko V., Khisbullin F. *Organohalogen Comp*, 2006; 68, p.354.
5. Seveso.20 years after.From dioxin to the Oak Wood.(Ramondetta M., Repossi A. Eds.), 1998, p.18-40.

TECHNOLOGY OF "*IN SITU*" BIOREMEDIATION OF SOILS CONTAMINATED BY PHOSPHORORGANIC PESTICIDES

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Large-scale use of phosphororganic pesticides and herbicides (POs) in agriculture in many countries has led to significant contamination of soils and crops grown on them. Currently, much attention is paid to soil fertility recovery. We believe the most promising means to be biotechnologies using special microorganisms-degraders. These biotechnologies are cost-effective and environmentally safe.

Studies within the ISTC #1892.2 Project are aimed at search and selection of microorganisms capable of degrading phosphoroorganic compounds by breaking direct C-P bond, and development on this basis of the technology for remediation of contaminated soils *in situ*.

MATERIALS AND METHODS

Isolation of microorganisms-PO degraders was conducted from soil samples taken in the territory of Moscow, Leningrad, Saratov, Volgograd, and Samara regions as well as from Krasnodar territory. The samples were taken near agricultural chemical storehouses, where the soil is contaminated by various fertilizers, phosphoroorganic pesticides and herbicides; on agricultural fields being processed with glyphosate (GP) for 2-5 years; near testing grounds where disposal of chemical weapons had been conducted. Biotesting of soil samples on daphnia showed high integral toxicity of the samples. Total amount of soil samples taken was more than 60.

Isolation of pure microorganisms' cultures, capable of degrading POs with direct C-P bond, was conducted on "rich medium" containing all the necessary nutrients, and on minimal salt nutrient media, where glyphosate or methylphosphonic acid in different concentrations served as a sole source of carbon.

Microfield trials were conducted on a specially allocated site using 2 strains of microorganisms-PO degraders. Soil on sites was ploughed up, loosen, and plant roots were removed. Then GroundBio was introduced in soil at a ratio of 100 l GP/hectare and kept for 2 days for in-soil processes stabilization. Microbial biomass was produced in fermenters on media of the same type. Before introducing microorganisms-degraders, soil was sampled for chemical analysis for glyphosate concentration, as well as for evaluation of total microbial contamination, phytotoxicity and integral toxicity study.

Chemical analysis of soil samples for glyphosate concentration was performed by gas-liquid chromatography method.

Soil samples were studied for saprophytic bacterial and fungal microflora, contamination by microorganisms-degraders, and dehydrogenase activity.

Soil phytotoxicity was assessed on oat germs using Berestetsky's technique.

Biotesting of soil aqueous extracts was conducted on daphnia *Daphnia magna* according to ISO 7346–1 international standard. Integral toxicity of soil extracts was assessed by daphnia mortality criterion. Biotesting on guppy fish was also conducted in compliance with ISO 7346–1. Toxicological trials were performed using a technique which doesn't implicate water change in the course of bioassay. Daily throughout the test the amount of survived fish was calculated and dead fish were removed.

STUDY RESULTS

1. Selection of strains of microorganisms-PO degraders.

At the first stage of laboratory studies microorganisms, capable of growing on nutrient medium containing glyphosate were isolated. The widest variety of strains was isolated from soil taken in southern regions of Russia (Samara and Saratov regions, Krasnodar territory), where the climatic conditions are more favorable and the concentration of soil microorganisms is higher.

At the second stage isolation of strains of microorganisms-PO degraders was conducted on MS1 mineral medium. This microbiological medium contains no organic compounds, but only mineral salts. At introduction of glyphosate in the medium it serves as a sole source of carbon, and on this medium only microorganisms, capable of degrading this substance and of using it as a sole source of carbon or phosphor, will grow.

The museum of microorganisms-COC degraders, containing 39 natural isolates of microorganisms-degraders of glyphosate and methylphosphonic acid was established.

2. Laboratory studies on COC degradation by the microorganisms.

Study of destructive properties of the selected strains of microorganisms-COC degraders and screening of the most active strains (by degradation ability) were conducted. Tests were performed both in liquid nutrient medium and in glyphosate-contaminated soils.

The primary criterion for assessment of strains-COC degraders was growth of biomass at cultivation in liquid mineral medium MS1 with GP (500 mg/l) or MFC (300 mg/l) and efficiency of these compounds' degradation. Degradation efficiency was demonstrated to increase with increase of initial GP concentration in the medium. Based on results of the microorganisms' growing on nutrient media with GP and MFC, for the further study on GP-contaminated soil 13 strains were selected.

At the next stage of selection, in laboratory conditions degradation of GP in soil with the use of the isolated strains was studied. Into glasses with water glyphosate was added and the content was treated with various strains of microorganisms. Degrading activity of the microorganisms was assessed by lowering of glyphosate concentration in soil and by integral toxicity. As a result of laboratory studies on glyphosate microbial degradation and for the further studies 7 most potential strains were selected.

3. Toxicological assessment of strains of microorganisms-degraders for safety for warm-blooded animals.

When isolating natural strains from the environment, a risk occurs to obtain microorganisms with toxic properties. Therefore, a critical point in the studies is assessment of the strains harmlessness for warm-blooded animals.

At the first stage of toxicological trials bioassay on daphnia was conducted. Bioassay results demonstrated that the tested strains at cultivation did not release exotoxins into nutrient medium, therefore, they are not toxic.

In compliance with the International GLP requirements assessment of the strains' harmlessness was performed on laboratory white mice and rats. Pathogenic properties of the isolated strains were assessed regarding the following indices of the test strains:

1. virulence – average lethal dose (LD_{50});
2. toxicity;
3. toxigenicity;
4. **dissemination in internal organs of experimental animals.**

As a result, 7 non-pathogenic for warm-blooded animals strains were selected. The microorganisms can be used in technologies for soil bioremediation without any limitations.

4. Field trials for the technology of bioremediation of PO-contaminated soils by means of microorganisms-degraders.

Microfield trials were conducted on a special test plot with the use of 2 most efficient and safe strains of microorganisms- PO degraders.

Concentration of glyphosate in soil in dynamics of the experiment was calculated as average value of 3 points in 3 repetitions. Results of chemical analysis demonstrated lowering of the concentration of introduced glyphosate under impact of microorganisms-degraders (Table 1).

Glyphosate content in soil in the course of microfield trials

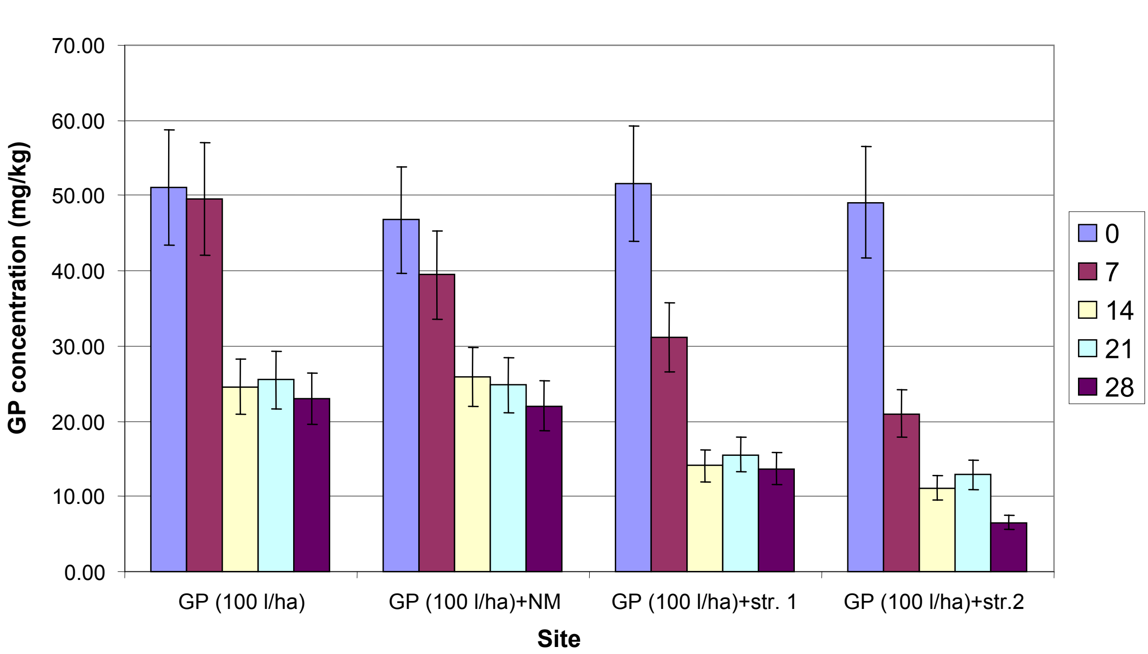
Table 1

Site characteristics	Glyphosate concentration in soil, mg/kg of abs. dry soil					Glyphosate degradation rate, %
	initial	1 week of bioremediation	2 weeks of bioremediation	3 weeks of bioremediation	4 weeks of bioremediation	
Pure soil (control)	0	0	0	0	0	--
Soil + GP 100 l/ha	51.10 ± 15%	49.57 ± 15%	24.60 ± 15%	25.50 ± 15%	23.00 ± 15%	55
Soil + GP 100 l/ha + nutrient medium	46.77 ± 15%	39.47 ± 15%	25.87 ± 15%	24.80 ± 15%	22.00 ± 15%	53
Soil + GP 100 l/ha + strain 1	49.10 ± 15%	20.97 ± 15%	11.13 ± 15%	12.90 ± 15%	5.43 ± 15%	89
Soil + GP 100 l/ha + strain 2	51.60 ± 15%	31.17 ± 15%	14.10 ± 15%	15.57 ± 15%	13.70 ± 15%	73

From Table 1 it follows that in all variants of the experiment, lowering of glyphosate concentration in dynamics of the experiment is observed. Natural loss of glyphosate for 28 days of the experiment made up 55%, that is a little more than half of the initial concentration. Adding nutrient medium in soil did not increase the degree of degradation; differences with control were not reliable. Adding strains-degraders statistically reliably enhanced degradation of glyphosate in soil up to 73% (strain 2) and 89% (strain 1), Fig. 1.

No migration of glyphosate in soil horizons in any variants of the experiment was observed during bioremediation.

Fig. 1. Dynamics of glyphosate degradation in soil



Phytotoxicity assessment of soil contaminated by glyphosate was performed before and after microbial remediation.

Glyphosate in dose 100 l/ha was phytotoxic for oats throughout the period of the field experiment. This was expressed in reliable decrease (1.5 times) of oats roots lengths compared to control (pure soil). During bioremediation, a reliable lowering of soil phytotoxicity was detected: on plots with nutrient medium – 1.3

times, with strain 1 – 1.5 times, with strain 2 – 2.9 times compared to GP-contaminated soil.

Quantitative control of microorganisms in soil during bioremediation demonstrated a slight change (because of the weather) of concentration of aboriginal soil microflora.

Quantity of microorganisms-degraders during bioremediation was gradually decreased.

Integral toxicity of soil contaminated by glyphosate before and after bioremediation was evaluated on daphnia *Daphnia magna.* Soil samples were taken on the day when microorganisms – degraders were introduced, after 7, 14, 21 and 28 days. Then water extracts were prepared. Bioassay results are presented in Table 2.

Integral toxicity of glyphosate-contaminated soil for daphnia, during bioremediation

Table 2

Site characteristics	Daphnia death, %				
	initial	1 week of bioremediation	2 weeks of bioremediation	3 weeks of bioremediation	4 weeks of bioremediation
Pure soil (control)	0	0	0	0	0
Soil + GP 100 l/ha	47	40	27	27	23
Soil + GP 100 l/ha	13	10	7	7	0
Soil + GP 100 l/ha + nutrient medium	47	27	27	20	20
Soil + GP 100 l/ha + strain 2	47	17	0	0	0
Soil + GP 100 l/ha + strain 2	13	7	0	0	0
Soil + GP 100 l/ha + strain 1	43	20	0	0	0

Dehydrogenase activity of soil is an indicator of soil microbial complex activity. Results of experimental studies (Fig. 2) demonstrated lowering of dehydrogenase activity of soil as a result of its contamination with glyphosate. Adding microorganisms-degraders facilitated restoration of biological properties of soil, i.e., its rehabilitation.

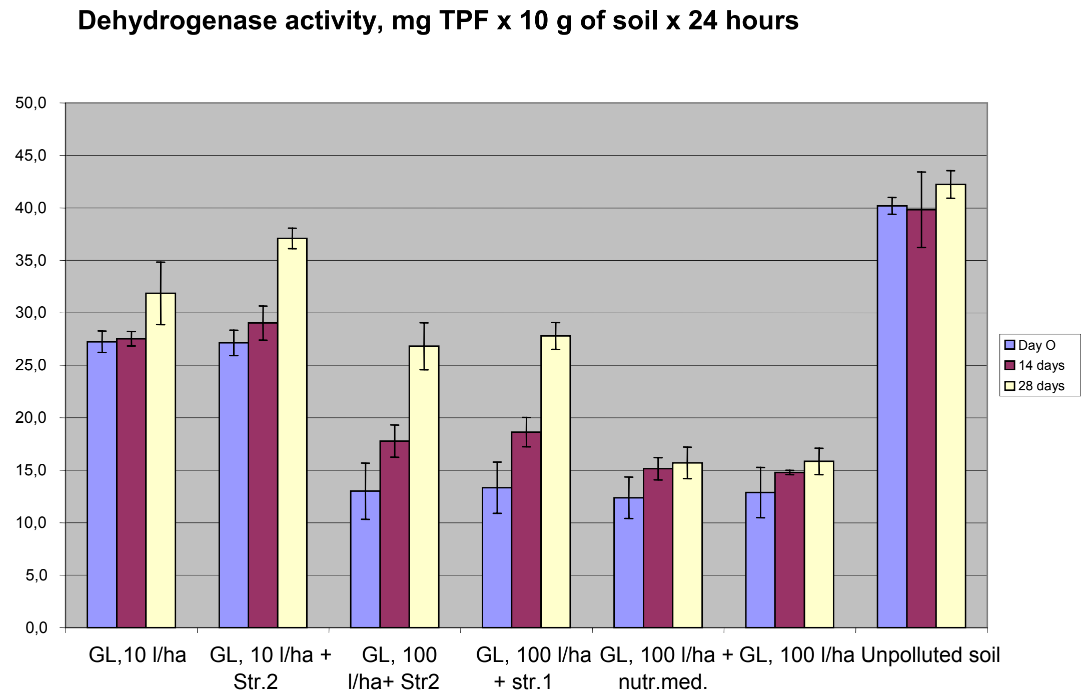


Figure 2. Soil dehydrogenase activity during bioremediation

Study of soil extracts' toxicity was conducted on white male rats. During the whole period of the experiment (up to 60 days) animals were given to drink only extracts from soil before and after bioremediation. The amount of consumed liquid and clinical state of animals was daily recorded. To make a complete evaluation of damaging effect of glyphosate and products of its hydrolysis on test animals, body weight and biochemical indices of blood and urine were weekly determined.

Results of toxicological studies demonstrated that glyphosate-contaminated soil after microbial bioremediation did not have toxic effect on laboratory animals.

Therefore, when conducting bioremediation of contaminated soil neither glyphosate degradation products nor introduced microorganisms-degraders are toxic.

CONCLUSIONS

Results of the experiments demonstrated that the isolated strains were able in different degrees to degrade COC in contaminated soil. Adding microorganisms in soil "*in situ*" provided 73- 89% degradation of glyphosate within a month.

At present, the work is being conducted on optimization of the main stages and schemes of the biotechnology application.

The study was carried out under financial support of the International Science and Technology Center (ISTC), project #1892.2.

ECOLOGO-TOXICOLOGICAL ASSESSMENT OF GLYPHOSATE'S IMPACT UPON AGROCENOSIS

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Broad-scaled and uncontrolled use of phosphorous-organic compounds (pesticides, herbicides, insecticides, etc) in agriculture caused considerable contamination of the environment with toxic compounds. Russia and a number of European countries currently are facing the problem of urgent eradication of unused pesticides and remediation of the contaminated soils. In order to eradicate phosphorous-organic compounds (POs) and to remediate contaminated areas physical, chemical and biological methods are used. Biological techniques are preferable being ecologically safe, less expensive and highly effective, which was repeatedly proved in course of completion other ecological tasks.

Currently the most problematic point in biotechnology of environmental protection is the problem of degradation of phosphorous-organic compounds with direct C–P bond wich is hard to hydrolyze (glyphosate or round–up, methyl-phosphorous acid and its analogies, methylphosphonic difluoride and others).

Glyphosate (GP) is one of the most frequently used herbicide in the world [Franz et al., 1997]. It is produced in form of 36% aqua solution of salt with isopropylamine, as it is for instance in case of the preparation Roundup-N, produced by Monsanto Co, or in the form of 50% powder (Phosulen) (Melnikov et al, 1985). It is nonselective herbicide of system action used for weeds' treatment following germination. GP is used on corps, in orchards (on fruit and citrus plants) on grapes and at target soil spraying (Melnikov et al, 1985), and in forests [Veiga et al., 2001]. As genetically modified plants (glyphosate resistant) are used more and more widely, toxic load upon agrocenoses increases and asks for more thorough study.

MATERIALS AND METHODS

Ecologo-toxicological studies of soil, contaminated with glyphosate was conducted in course of field studies of biotechnology. The technology of bioremediation *«in situ»* of soils, contaminated with glyphosate was developed at RCT&HRB. In course of long-term laboratory studies microorganisms glyphosate degraders were isolated from contaminated soils and characterized. Most effective ones and safest for warm-blooded animals strains were selected.

Microplot field trials were conducted on a target field with use of 2 strains POs degraders. The soil was ploughed, roots were eradicated, the soil was moldered. Then "Ground Bio" was introduced in soil at 100 l GP/hectare and left for 48 hours to let intra-soil processes get stabilized.

Microbial biomass for bioremediation was simultaneously accumulated in fermenters on nutrient medium of similar type. The suspension was introduced into soil at 1 liter per 1 m^2.

Prior to introduction of microorganisms degraders soil samples were taken for chemical assay, total bacterial number assessment, phytotoxicity and integral toxicity assessment.

Chemical assay of soil specimens for glyphosate occurrence was conducted with use of X gas-liquid chromatography.

Soil specimens were studied for saprophyte, bacterial and fungi micro-flora, for microorganisms-degraders number and for dehydrogenase activity. For microbiological studies an aggregated weight of 5 gram was taken from the soil specimens. First dilution of soil was prepared in flasks and intensively shaken for 10 minutes, after that 10-fold dilutions were prepared up to 10^{-6}. Inoculation was conducted from 10^{-3}- 10^{-6} dilutions on Petri dishes with agarized FHFF medium. The microorganisms' growth was registered 2 days following cultivation at (28±1)°C. The data were processed with humidity rate taken into account.

Phytotoxicity of soil was assessed on the oats' sprouts with use of Berestetsky's method. Soil specimens

50 g of weight were put into Koch dishes, covered with two layers of filter paper and wetted with settled tap water. On the surface of filter water 50 oats' seeds were put. Morphometric parameters (sprouts' and roots' length, sprouts' weight) were measured after 5 days. Soil specimens causing decrease in seeds' vitality or inhibition of sprouts' and roots' growth by at least 30 % compared to the control were considered toxic.

Biotesting of water soil extracts was conducted on *Daphnia magna* according to international standard ISO 7346–1. To conduct assays water extracts were prepared from soil. Integral toxicity of soil extracts was determined by loss in daphnia. The losses were assesd in dynamics in 1, 6, 24, 48, 72 and 96 hours.

Biotesting on guppy fishes was also conducted by ISO 7346–1. Toxicological tests was conducted with use of the technique, where the solutions were not changed during all the period of biotesting. During all the testing period the number of survived and dead fishes was counted daily. Dead fishes were taken out.

TEST RESULTS

1. Study of glyphosate degradation in course of microbial bioremediation.

The results of chemical assays demonstrated that microorganisms-degraders cause a considerable decrease in concentration of glyphosate introduced in soil, Table 1.

Glyphosate concentration in soil in dynamics of the field trials

Table 1

Time (days)	soil + GP (control)	soil + GP + nutrient medium		soil + GP + st. 1		soil + GP + st. 2	
	Average concentration, mg/kg	Average concentration, mg/kg	% of control	Average concentration, mg/kg	% of control	Average concentration, mg/kg	% of control
0	107.22 ± 6.32	107.22 ± 6.32	100.00	107.22 ± 6.32	100.00	107.22 ± 6.32	100.00
2	71 ± 2.92	71 ± 2.92	100.00	71 ± 2.92	100.00	71 ± 2.92	100.00
9	51.33 ± 8.22	50.11 ± 4.84	97.62	29.33 ± 2.17	57.14*	37.22 ± 2.32	72.51
16	53.56 ± 6.33	56.22 ± 5.59	104.98	33.13 ± 1.22	61.85*	33.33 ± 4.28	62.24
30	50.78 ± 4.25	42.67 ± 3.30	84.03	25.56 ± 2.07	50.33*	34.44 ± 0.69	67.83*
Degr.degree, %	52	60		76		68	

According to Table 1, in all the variants of the experiment concentration of glyphosate goes down in the dynamics of the experiment. Natural loss of the preparation during 30 days of experiment came up to 52%, i.e. exceeding a little half of initial concentration. Introduction of nutrient medium into soil only slightly increased the degree of degradation (up to 60%), but the differences with control were not reliable. Introduction of strain-degraders contributed to glyphosate degradation in soil up to 68% (strain 1) and 76% (strain 2), Fig.1.

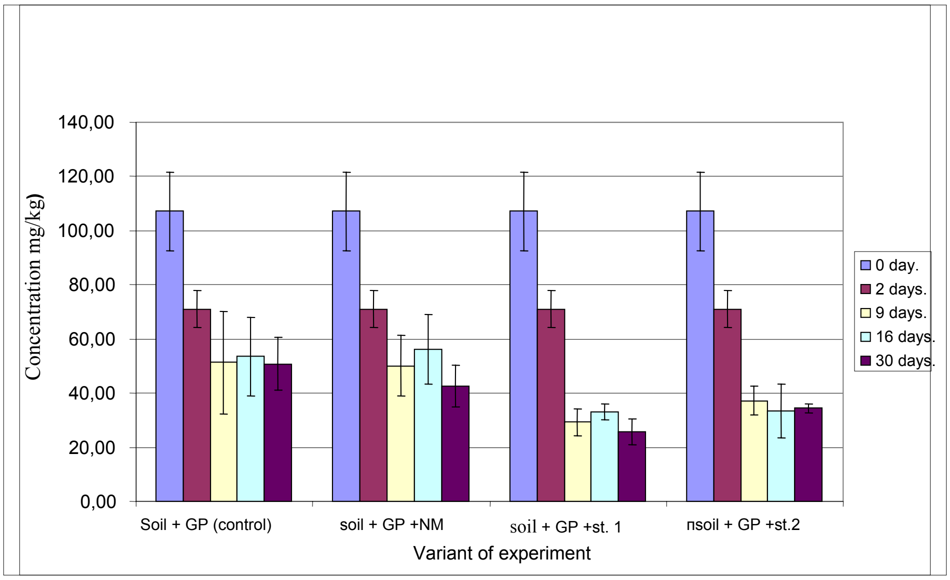

Figure 1. Dynamics of glyphosate degradation in soil in course of field experiment

The analysis of the glyphosate degradation dynamics by introduced microorganisms allowed for the conclusion that decrease in preparation's concentration in soil was reliably higher (1,6 – 2 times as high), compared to control.

2. Study of the dynamics in the number of microorganisms introduced in soil in course of microbial bioremediation.

The results of microbiological studies of soil in course of bioremediation are presented in Table 2.

The number of microorganisms- degraders of glyphosate in soil in course of bioremediation

Table 2

Soil specimen	Number of microorganisms, CFU/1g abs. dry soil			
	initial	7 days	14 days	30 days
Soil + glyphosate + strain 1	$(2.15\pm0.19)\cdot10^7$	$(9.3\pm1.30)\cdot10^5$	$(7.0\pm1.61)\cdot10^4$	$(1.0\pm0.21)\cdot10^5$
Soil + glyphosate + strain 2	$(1.46\cdot\pm0.17)\cdot10^8$	$(6.2\pm1.72)\cdot10^5$	$(2.1\cdot0.19)\cdot10^5$	$(1.3\pm0.19)\cdot10^5$
Soil + glyphosate + nutrient medium	0	0	0	0
Soil + glyphosate	0	0	0	0
Pure soil	0	0	0	0

The introduced amount of strain-degraders, determined by inoculation from soil was rather high and came up to 10^7-10^8 cells per 1 gram of dry soil. In course of the experiment changes in concentration of microorganisms were observed: on the 7th day of the experiment concentration of strains degraders considerably fell up to 10^5-10^6 viable cells per 1 gram of dry soil due to dry hot weather, in a month the concentration of strain 1 fell down to 2 orders of magnitude while the concentration of strain 2 fell down to 3 orders of magnitude.

But of a special interest is the correlation between glyphosate concentration in soil and the parameters to characterize biological activity of the soil, which are integral toxicity, biomass of the soil bacteria, dehydrogenase activity and phytotoxicity.

3. Biotesting of soil specimens, selected in course of microbial bioremediation on daphnia.

Integral toxicity of soil, contaminated with glyphosate prior to and during bioremediation was assessed on laboratory culture of *Daphnia magna*. Soil specimens were taken on the same day of microorganisms-degraders introduction into soil, after 7, 14 and 30 days.

The results of biotesting are presented in Table 3.

The assessment of integral toxicity of the soil, contaminated with GP in course of bioremediation

Table 3

Soil specimen	Daphnia loss to control, %			
	initial	7 days	14 days	30 days
Soil + glyphosate + strain 1	60	27	10	0
Soil + glyphosate + strain 2	63	30	13	0
Soil + glyphosate + nutrient medium	67	53	40	34
Soil + glyphosate	60	47	43	40
Pure soil (control)	0	0	0	0

As the result of the experiment it was established that on the 30th day following bioremediation there was no loss of daphnia in soil processed with microorganisms, where in the soil contaminated by glyphosate the losses came up to 40%.

4. Biotesting of soil specimens selected in course of microbial bioremediation of soil on guppy fishes.

The results of biotesting on guppy fishes showed that water extracts obtained from soil samples prior and following bioremediation are not toxic for these test articles.

5. Study of phytotoxicity of soil specimens.

Phytotoxicity of contaminated with glyphosate soil specimens prior to and following bioremediation was assessed on oats' sprouts under laboratory conditions, Table 4 and 5.

The assessment of phytotoxicity of the soil contaminated with glyphosate prior to bioremediation

Table 4

Variant of the experiment	Number of sprouts		Average length of the roots		Average length of sprouts		Sprouts' weight	
	items	% to control	Mm	% to control	mm	% to control	Gram	% to control
Soil + glyphosate + strain 1	47	109	25.7 ± 1.3	134	30.1 ± 1.5	157	5.21 ± 0.25	145
Soil + glyphosate + strain 2	48	112	26.4 ± 1.4	137	29.2 ± 1.5	153	5.38 ± 0.36	150
Soil + glyphosate + nutrient medium	45	105	19.4 ± 1.0	96	24.6 ± 1.3	129	4.45 ± 0.20	124
Soil + glyphosate	43	100	20.6 ± 0.9	102	22.7 ± 1.3	119	3.76 ± 0.13	105
Pure soil (control)	43	–	20.2 ± 0.9	–	19.1 ± 1.2	–	3.59 ± 0.17	–

As Table 4 shows, introduction of Ground-bio in the soil of test plots did not result in phytotoxic effect. All morphometric indices of oats, germinated on the soil contaminated with glyphosate were of the same order of magnitude as those in control (pure soil).

Soil specimens after bioremediation in all the variants of the experiment also did not impose any negative effect upon germination and development of oats plants.

Thus, in course of microbial bioremediation of soils neither glyphosate degradation products, nor introduced microorganisms degraders possess any phytotoxicity.

7. The evaluation of the effect caused by microorganisms-degraders' introduction in soil upon aboriginal soil microflora.

In course of the field trials the effect caused by microorganisms-degraders' introduction in soil upon aboriginal soil microflora and its biological state (by dehydrogenase activity) was assessed.

A) Bacterial and fungal biomass measurement in soil, contaminated with glyphosate in course of microbial bioremediation

In order to measure bacterial and fungal biomass soil suspension (1:10) was prepared and processed with supersonic sound of 22 кHz, 0,4 A; 2 min. It settled 2 ml of suspension from the middle part was taken out and then taken to flask with 18 ml of sterile water. Then the suspension was applied with micropipette on the degreased slides. The number of bacteria and fungi was calculated on the same preparations (Methods of soil microbiology in biochemistry // Edited by D.G. Zvyagintseva- 1991).

In the process of calculation of soil bacteria complexes the preparation were stained with aqua solution of acridine orange; for mycelium calcofluor white. The results of bacteria counting were given in terms of million cells per 1 gram of abs. dry soil. The length of mycelium was calculated and given in terms of meters per 1 gram of abs. dry soil Biomass was calculated taking into account that biomass of the dry substance of a bacterial cell of 0.1 μm^3 is $2x10^{-14}$ gram, 1 m of fungial mycelium 0.5 μm of diameter is $3.9x10^{-6}$ gram (P.A. Kozhevin// Population ecology of soil microorganisms. Doctoral theses - 2000).

The results of field trials of microbial remediation of soil showed that microorganisms-degraders' introduction contributes to rise in biomass of bacteria and fungi in glyphosate contaminated soil. Thus, introduction of biodegraders into contaminated soil was accompanied by increase in biomass of bacteria and fungi 1.2–1.3 times as high and 1.5–1.6 times correspondingly, Fig. 2 and 3.

Increase in biomass of the main groups of soil microorganisms indicates the decrease in toxic load upon soil microbiocenosis in course of microbial remediation of soil.

B). Determination of dehydrogenase activity in glyphosate-contaminated soil in the course of microbial bioremediation.

The results of experiments showed that contamination of soil by glyphosate leads to decrease in its dehydrogenase activity. Activity of dehydrogenase in pure sod-podzol soil at the beginning of experiment was 40.4 mg TPF per 10 g of soil in 24 h, whereas in experiment variants with glyphosate this value varied within the range of 13.3-16.1.

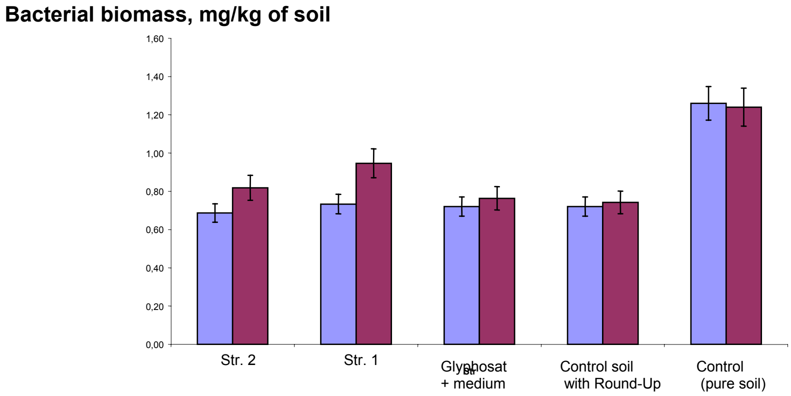

Figure 2. Biomass of bacteria in contaminated with glyphosate soil in course of bioremediation

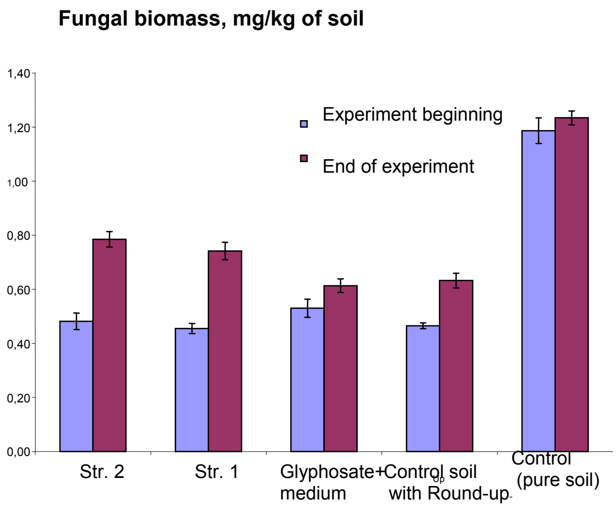

Figure 3. Biomass of fungi in the soil contaminated with glyphosate during bioremediation

After 1 month of experiment soil dehydrogenase activity in control variant was practically at the same level, and in variants with glyphosate – increased (Fig. 4). The highest increase in dehydrogenase activity was noted in test variants implicating introduction of microorganisms-degraders: 1.9 and 2.1-fold for strains 1 and 2, respectively. Therefore, microbial remediation of glyphosate-contaminated soil is accompanied with the increase of its dehydrogenase activity.

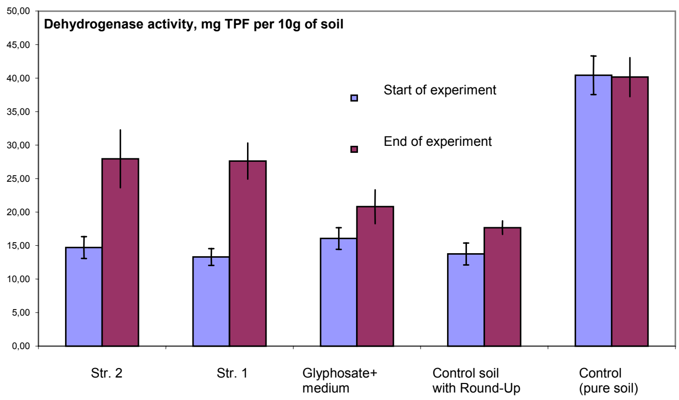

Figure 4. Soil dehydrogenase activity in the course of bioremediation

The study results showed that the introduced glyphosate has negative impact on soil properties. Integral toxicity increase, decrease in amount and biomass of saprophytic bacteria and fungi, as well as decrease in dehydrogenase activity were noted.

Microbial bioremediation of glyphosate-contaminated soil results in soil biological activity recovery.

CONCLUSIONS

1. Introduction of glyphosate in soil has negative impact on its biological properties. Integral toxicity increase, decrease in amount and biomass of saprophytic bacteria and fungi, as well as decrease in dehydrogenase activity were noted.
2. Bioremediation of contaminated soil by means of microorganisms-degraders was accompanied by the increase in biomass of saprophytic bacteria and fungi 1.2–1.3 and 1.5–1.6 times respectively (practically the level, typical for pure soil). The increase in biomass of the main groups of soil microorganisms points out the decrease of toxic load on soil microbiocenosis in course of microbial remediation.
3. Microbial bioremediation of soil contaminated with phosphoroorganic compounds is environmentally safe and leads to soil fertility recovery.

The study was carried out under financial support of the International Science and Technology Center (ISTC), project #1892.2

SYNERGY BETWEEN PLANT ROOT AND RHIZOSPHERE MICROORGANSMS TO ENHANCE BREAKDOWN OF POP EXAMPLIFIED WITH ATRAZINE AND ITS METABOLITES

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The fact that farm production needs to be maintained not at present level but must be increased to higher levels to provide the quantity, quality and safety of food required for the increasing world population. Obviously this will require high inputs including chemicals to sustain the production. The fact remains that environment friendly biopesticides are not able to give either guarantee for safe production or not developed enough to protect crops from different pests and diseases. Farmers are left to use chemical pesticides, although many of them are environmentally unsafe. Author has attemted to degrade both pesticides through Plant Root system alone, Rhizosphere Microorganisms alone and a mixed Plant Roots –Rhizosphere-Microorganisms in simple model systems and under complicated field conditions as well. Following are important outcome:

Phytostimulation and bio-phytoremediation seems the most promising approach to remove atrazine through Vetiver; it has been tested under field condition in small-scale experiment and is ready to be verified in large field experiments.

The use of Vetiver to remove atrazine from contaminated soils or to reduce the risk of runoff of the herbicide is ready to be tested at large scale**.**

Key words: Rhizoshere, HCH, Atrazine, mineralization, root-rhizospher soil- interaction, Soil-root-interaction, rhizosphere, bioaugmentation

Introduction

On a global scale the concept of food safety and security has been increasingly refined over the last 50 years. After World War II, food security meant physical availability of sufficient food. After the onset of the Green Revolution in the sixties, economic access of food at the household level was included in the concept of food security, to which then also the component of social justice was added. With the UN Conference on Environment and Development held at Rio de Janeiro in 1972 environmental issues became increasingly important in addition. In recent years the scandals relating to food poisoning and misuse of agriculture for the disposal of organic wastes containing hazardous substances and pathogens have created new concern about food safety in increasingly industrialized agricultural production systems and a globalised market of food products, and led to an increased consciousness of consumers with respect to toxic substances, endocrine disruptor residues of pharmaceuticals, pathogens, genetically modified crops.

In order to prevent widespread use of pesticides in intensive agriculture and public health , FAO has suggested a preventive Food Safety System for both developed and developing countries. Based on this system, the responsibility for providing safe food should be shared by all players in the food and agricultural sector, from food producers and processors to retailers and consumer households.

In these circumstances, agriculture food producers have a great responsibility to maintain sustainable soil quality in the long-term, which is directly affected by the degree of intensity of agricultural land use and its management. Once soil quality is damaged, it is very difficult or even impossible to repair. Intact soil performs vital ecological functions by filtering and inactivating pollutants, decomposing organic waste substances, and recycling nutrients. But, if the retention and filtering capacity of a soil becomes exceeded, it can become a source of pollutants and undesired substances entering the food chain. High contaminant levels for groundwater, surface water, agricultural products and agricultural soils were recorded and documented worldwide. The question raises how agriculture can define and warrant the quality of soil and plant products in future. Obviously, such a goal can only be achieved by ecologically and economically viable agricultural land-use to maintain the recreational value of the landscape and ensure life-supporting ecological functions.

Rationale

However, the problem with already contaminated sites persists. The fact that farm production needs to be maintained not at present level but must be increased to higher levels to feed quality food for increasing population. Naturally this will require high inputs i.e. water, fertilizers, and plant protection through chemical and biopesticides. The fact remains that environment feiendly biopesticides are not developed to protect all crops from pests and diseases.

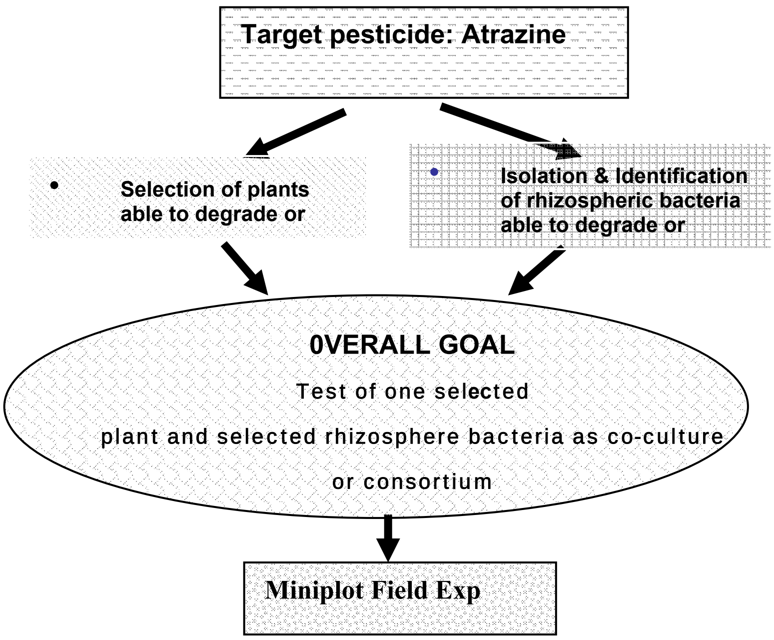
Several methods are currently in use to decontaminate polluted soils, but the majority are based on ex situ chemical inactivation or thermal degradation. 'Harsh' remediation techniques such as soil washing, incineration, thermal treatment, electro-migration, vitrification, or excavation and reburial, however, do not only destroy the ecological soil quality, they are often also too expensive for agricultural land and should therefore only be applied in rare cases where high risks exist. In order to restore large areas of contaminated soil, 'gentle' remediation techniques are required. A promising approach is phytoremediation using the interactive potential of plant and microbial activities in the rhizosphere to remove pollutants

Strategie /Concepts

In an Integrated Research Project financed by funds made available by the Indo-Swiss Colloboration in Biotechnology is to develop better understanding of soil-plant interaction either to extract or to degrade or to stabilise atrazine and their metabolites in sites exceeding Maximum contaminant Levels Goals (MCLG). There are no systematic studies on Soil –Plant Interaction exist in literature

In this project selection of plants that can remove or degrade the target pesticides; delineation of metabolic pathways employed by plants; isolation of rhizospheric bacteria; conduct lab, pot and mini-plot experiments; and risk assessment with respect to pesticides hexachlorocyclohexane and atrazine.

Figure 1. Development of Field Applicable Phytoremediation Technique for two Pesticides



2. Materials and Methods

In order to establish the importance of soil-Plant interaction in field condition, laboratory. greenhouse studies on degradation and transformation of atrazine and their metabolites are planned with the selected plants and their rhizospheric co-culture or consortium. Two different analytical techniques bio-chemical and radio tracer are used for these studies:

3. Result and discussion

3.1. Investigation to select plants can survive at 2 ppm of Atrazine Conc in soil

In one pot culture experiment agricultural and non-agricultural plant species for resistancfe to Atrazine. Are investigated. Seeds/seedlings of around 5 agricultural and 10 non-agricultural plant species were tested for growth in 2 ppm atrazine spiked black cotton soil in porcelain pots. Two non-gricultural and two agricultural plant species e.g. Gliricidia, and Vetiver , corn and sugarcane proved to tolerant.

3.2 Investigation to assess the atrazine degrading capability of corn plants in Black cotton soil

For soil experiments under green house condition 10 kg black cotton soil was used in porcelain pots. Soil was spiked with 2 ppm atrazine. Seeds were used for experiment and growth of the plant was monitored from germination upto one month. Residual atrazine was extracted from soil with methanol and analyzed by HPLC. Vetiveria plants having 30 gm. weight were planted in each pot. One pot was not spiked with atrazine, which served as positive control. The experiment was run in triplicate with appropriate controls (soil + atrazine, no plants, soil + plants, no atrazine) kept in green house throughout the experiment.The corn plant showed 70% degradation of atrazine from soil during one month of growth. Microorganisms have been isolated from corn rhizosphere and tested for degradation of atrazine.

3.3 *Investigation to assess the atrazine degrading capability of vetiveria plants in hydroponics*

After 30 days of incubation period complete removal of atrazine from hydroponics system with Vetiveria plant was observed. In hydroponics system without vetiveria plants, 14 % removal was observed.. There was no difference in biomass also. No change was observed in pH of the hydroponics solution during the experiment. The experiment indicated uptake of atrazine by Vetiver plant system

3.4 Uptake of ^{14}C Atrazine by Vetiveria plants in hydroponic medium

The experiment indicated uptake of atrazine by Vetiver plant (Table 1)

Percent Distribution of ^{14}C Atrazine residues in *Vetiveria* plants

Table 1

Treatment	Percent ^{14}C residues in						
	Hoagland Solution	Shoot	Root	Bottle Washings	Root Washings	Foam (Volatilization)	Total
Unsterilized Conditions:							
Control (No Plant)	101	----	----	0.37	----	0.1	102
Plant exposed for 15 days	57	22.4	11.6	0.1	1.7	0.0	93
Sterilized Conditions:							
Control (No Plant)	101	-	-	0.1	-	0.5	102
Plant 15 days Exp	74	20.0	8.8	0.1	1.3	0.0	105

Results in Table 1 shows that a major portion of Atrazine is accumulated in roots and shots.

3.5 Investigation to assess the amount of degradation of Atrazine in Black cotton Soil:

An experiment was conducted with glass bottles filled with 100 g. black cotton soil spiked with 4 ppm atrazine. Following experimental sets were established in triplicate (Table 2).

After 15 days of atrazine exposure, atrazine was extracted from all experimental sets with dichloromethane. HPLC analysis was done to determine residual atrazine concentration.

3.6 Investigation to assess the atrazine removal capability of vetiveria *Vetiveria zizanioides)* plants in Black cotton soil at 4 ppm

After 15 days of atrazine exposure, atrazine was extracted from all experimental sets with dichloromethane. HPLC analysis was done to determine residual atrazine concentration.

The results (Table 2) indicate that after 15 days of period, Vetiver has removed atrazine (below detection limit of 10 ppb.) from soil. Unsterile soil has showed 36 % removal of atrazine from soil. Thus indigenous micro flora was responsible for 36 % removal of atrazine but in presence of Vetiver complete removal was observed. This enhanced removal may be due to increase in microflora in rhizosphere of Vetiver and removal by Vetiver itself. Thus Vetiver grass holds great potential in phytoremediation of atrazine from soil.

Table 2

Atrazine Dose ppm	Treatments			
	1	2	3	4
	Sterile soil	Unsterile soil	Sterile Soil + vetiver	Unsterile soil + atrazine+Vetivier
Atrazine 4 ppm	4.4	2.8	0	0

3.7 Plant roots (Vetiveria) –microbial interaction for remediation of atrazine contaminated soil.

500 g. black cotton soil filled in 1 L. capacity glass bottles was spiked with commercial atrazine formula-

tion (Altrataf,Rallies India Limited) at 25 ppm (AI) concentration. Atrazine degrading bacterial culture was added at 10^8 CFU/g density in the form of black cotton soil based bioinoculum prepared in earlier experiment.

Plants: Vetiveria plants of average 3 months age were purchased from BAIF, Pune. 100 g. biomass of Vetiver plants were planted in 500 g. black cotton soil filled in 1 L. capacity glass bottles. Plants were allowed to establish for 15 days. All the plants were watered regularly. Experimental set up

Vetiveria (*Vetiveria zizanioides*) was found to be resistant to atrazine and capable of removing atrazine from soil and hydroponics medium during our study. Bacterial culture R2 (*Arthrobacter* sp.) capable of atrazine degradation was isolated from rhizosphere of Vetiver plant. It has shown capacity to remove atrazine from contaminated soil. Interactive potential of Vetiveria and bacterial culture isolated from its rhizosphere was tested for atrazine removal from soil. Following conclusions are drawn:

- After 4 days of atrazine exposure, the soil planted with Vetiver along with bacterial culture showed complete removal of atrazine.
- Vetiver plants alone showed 31 % atrazine removal from soil.
- Bacterial culture was able to remove 94 % atrazine from unsterile soil.
- Plant microbial interaction showed rapid atrazine removal when compared with culture and plants alone. When comparing the results of the 3 rd day, culture and plants alone showed 65 % and 24 % atrazine removal respectively, plant-microbial interaction showed 80 % atrazine removal.
- Sterile soil spiked with atrazine showed 6 % atrazine removal after 5 days of exposure, which could be accounted for adsorbtion and other physical factors.
- Normal flora of soil contributes to14 % atrazine removal.

3.8 Investigation to assess the highest atrazine concentration tolerated by Veteveria

To attain active ingredient concentration in range of 50 ppm to 15000 ppm. 10 porcelain pots were filled with 10 kg soil spiked with gradient of atrazine concentration. Vetiveria plants having 30 gm weight were planted in each pot. One pot was not spiked with atrazine, which served as positive control

All the Vetiveria plants were not exposed to atrazine before the experiment. Effect of atrazine was noted on the basis of wilting of leaves, retardation of growth, new offshoots etc.

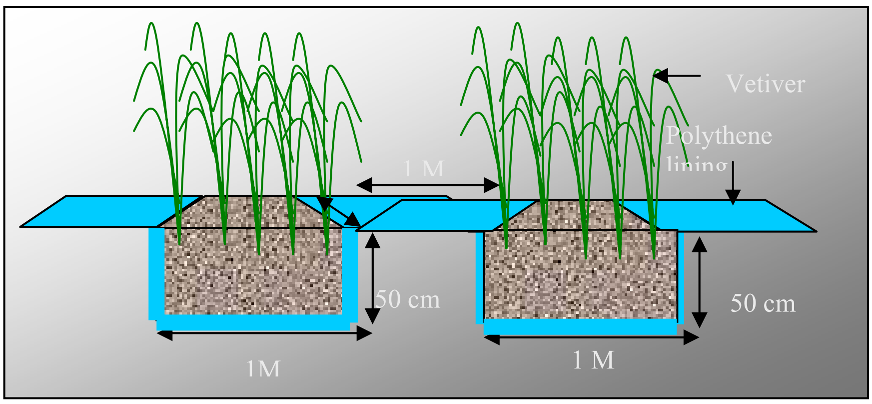
Results showed that growth of Vetiver was not adversely affected by application of atrazine up to 10000 ppm atrazine. It showed some wilting effect and retardation of growth of Vetiver at 15000 ppm application. Thus Vetiver can be used at atrazine accidental spill sites for phytoremediation. Removal of atrazine from soil with the help of Vetiver at high concentration will prove its potential for phytoremedaition.

Evapotranspiration losses were same in exposed and unexposed plants. There was no retardation of growth of Vetiveria exposed to atrazine as compared to control Vetiveria plants. There was no difference in biomass also.

No change was observed in pH of the hydroponics solution during the experiment

3.9 Microplot Field Experiment

Figure 2: Diagrammatic representation of field experimental plot



Treatments

1. Soil not spiked with atrazine, planted with Vetiver plants (vegetation control).
2. Soil spiked with atrazine, planted with Vetiver plants.

3. Soil spiked with atrazine, planted with Vetiver plants & atrazine degrading culture.
4. Soil spiked with atrazine and atrazine degrading culture (Arthrobacter sp. isolated from rhizosphere of Vetiver plant exposed to atrazine, at 108 cells/ g soil).
5. Soil spiked with atrazine (no vetiver, no atrazine degrading culture).

The treatments were initiated after the plants got established in field soil. The experiment was done in duplicate.

Sampling – Soil sampling from all experimental plots was done on 0 h, 2nd day, 4th day, 7th day, 10th day and 15th day.

Atrazine estimation – Atrazine was extracted from soil in dichloromethane and estimated by HPLC as described earlier.

Soil characterization – The field soil was characterized for pH.

Figure 3.: Field scale experiment for phytoremediation of atrazine contaminated soil using Vetiver plant

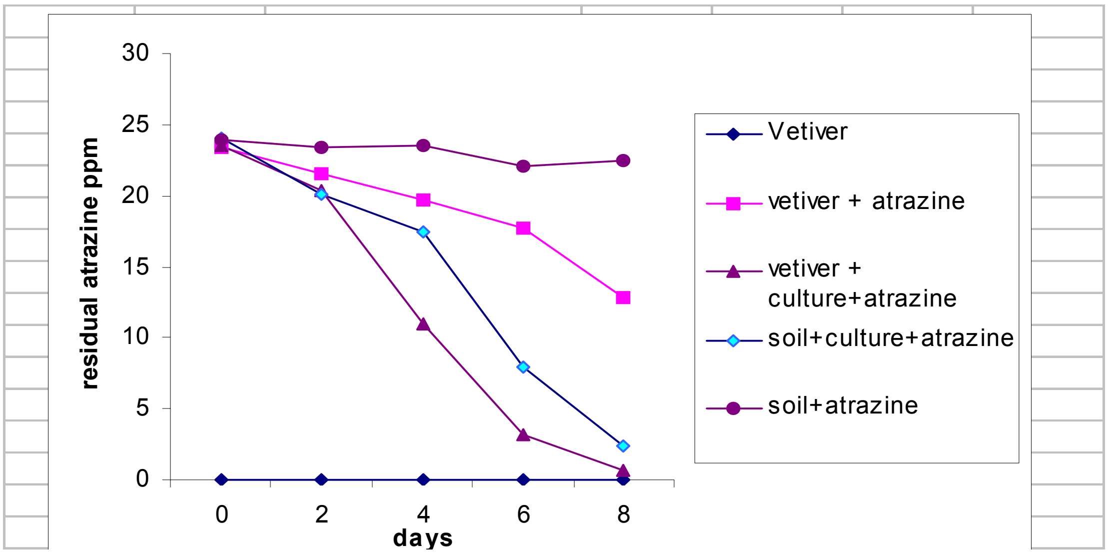


Figure 4: Vetiver microbial interaction for removal of atrazine from field soil

It was seen that while Vetiver plant alone removed 45% atrazine from soil, Vetiver plant + culture removed 98% atrazine from soil. To culture alone removed 90% atrazine from soil and indigenous flora of soil removed 6% atrazine from soil. Thus Vetiver plant microbe interaction enhanced removal of atrazine from soil.

The field experiment thus confirmed that the Vetiver plant could be used as a model for phytoremediation of atrazine contaminated soil and plant microbe interaction would enhance removal of atrazine from soil.

3.9 Effect of bioaugmentation of atrazine spiked soil with atrazine degrading culture on growth of atrazine sensitive leguminous plant.

Based on results of bench scale experiments on survival of leguminous plants in atrazine spiked soil bioaugmented with atrazine degrading culture, field scale experiments were set at VSI, Pune.

Materials and Methods

The experimental plots were identical to that used for phytoremediation of atrazine contaminated soil using Vetiver plant – microbe interaction. Vigna plants were used for experiments.

Figure 5: Field experiments to see effect of bioaugmentation of atrazine contaminated soil with atrazine degrading culture on the growth of Vigna sp.

Treatments:

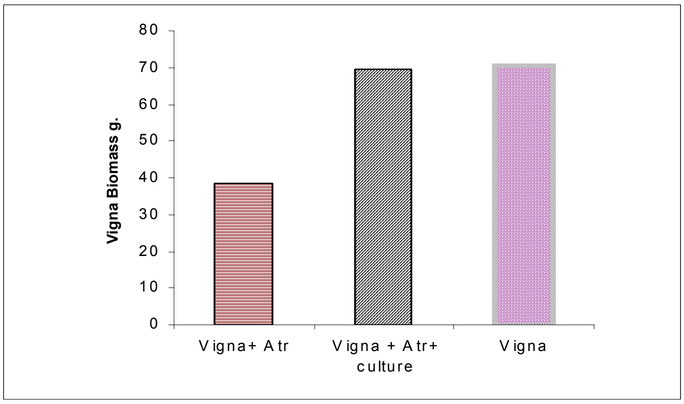
1. Soil not spiked with atrazine but planted with leguminous plants.
2. Soil spiked with atrazine and planted with leguminous plants.
3. Soil spiked with atrazine and amended with atrazine degrading culture and planted with leguminous plants.

200 seeds of legumes were sown in the soil and sampling was done after 15 days for biomass of leguminous plants grown and residual atrazine from soil.

Results and Discussion

Vigna biomass in presence of Athrobacter sp. in atrazine-spiked soil (69.7 g) is equal to the Vigna biomass (70 g) in soil without atrazine. 46% reduction in Vigna biomass was observed in soil with atrazine, without supplement of atrazine degrading culture.

Figure 6: Effect of atrazine degrading bacteria on survival of Vigna in atrazine spiked soil



It is seen that there was normal growth of Vigna in sets receiving bacterial culture while wilting and growth retardation in Vigna plants receiving no culture. Survival of Vigna plants in atrazine treated soil bioaugmented with atrazine degrading culture proved efficiency of the culture to remove atrazine from soil.

References:

1. Chaudhry Q., M. Blom-Zandstra S.K. Gupta and E. Joner, 2005. Utilising the synergy between plants and rhizosphere microorganisms to enhance breakdown of organic pollutants in the environment. ESPR-Environ Sci & Pollut Res 12 (1) 34-38, (2005).www.scientificjournals.com
2. Mirgain G., Green A. and Monteil H. 1993. Degradation of Atrazine in Laboratory Microcosms Isolation and Identification of the Biodegrading Bacteria." Environmental Toxicology and Chemistry Vol.12, p. 1627-1634
3. Wackett L.P., Sadowsky M.J., Martinez B., Shapir N. 2002. Biodegradation of atrazine and related s-triazine compounds: from enzymes to field studies.Appl Microbiol Biotechnol. Jan;58(1):39-45.
4. Hanson J.E., Stoltenberg D.E. , Lowery B. and Binning L.K. 1997. Influence of Application Rate on Atrazine Fate in a Silt Loam Soil. J. Environ. Qual. 26:829.