10TH INTERNATIONAL HCH AND PESTICIDES FORUM

„How many obsolete pesticides have been disposed of 8 years after signature of Stockholm Convention“

BOOK OF PAPERS

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Section 1: HCH and other pesticides global and regional problems

HCH GLOBAL STRATEGY
UNEP-UNIDO PROGRAM CONCEPT FOR SUBMISSION TO GEF- THE GLOBAL ENVIRONMENT FACILITY

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This paper explains the first outlines on the HCH Global Strategy Program concept that will submitted soon to the Global Environment Facility. It explains briefly the need for a global strategy on dealing with HCH waste. The amounts are huge and the solutions are complex not clear yet.

The information is on HCH waste is very old, and in most of the countries the production of Lindane and the corresponding generation of HCH-waste has not been documented very well. Additionally the persons that have extensive knowledge about production and the related waste locations are often very old and most of them are not alive anymore and therefore, this makes the historical investigation not an easy task.

Luckily, IHPA has collected over the last years, with limited or no means, a considerable amount of information on a large number of Lindane production sites and HCH waste storage locations. IHPA therefore submitted to the Secretariat of the Stockholm Convention in 2006 „The Legacy of Lindane HCH Isomer Production“ (see http://www.ihpa.info/resources/library/), which has been used as major information source on the final decision to list HCH as a POP. However the study, can only be used as a base and more and detailed information is needed for a good global overview, and therefore more works have to be implemented to assess if there are more locations as indicated in the report and a detailed verification of estimated amounts of HCH –waste have to be made. Some of the first ideas on inventory works, based on a number of cases that have been documented very well and has been presented in the same session in Brno by Dr. Roland Weber together with Prof. Rul Lal. It is planned that IPEN will work on this issue during the program. In any case, one can state that next to the volumes on the globe, information on the quality of the HCH will be part of the investigation works. It is expected that there are different locations:

- those with pure HCH-isomers (alpha, beta and delta) and frequently in combination with Hg generated form the chlore alkali process, but also
- where HCH has been disposed together with other wastes.

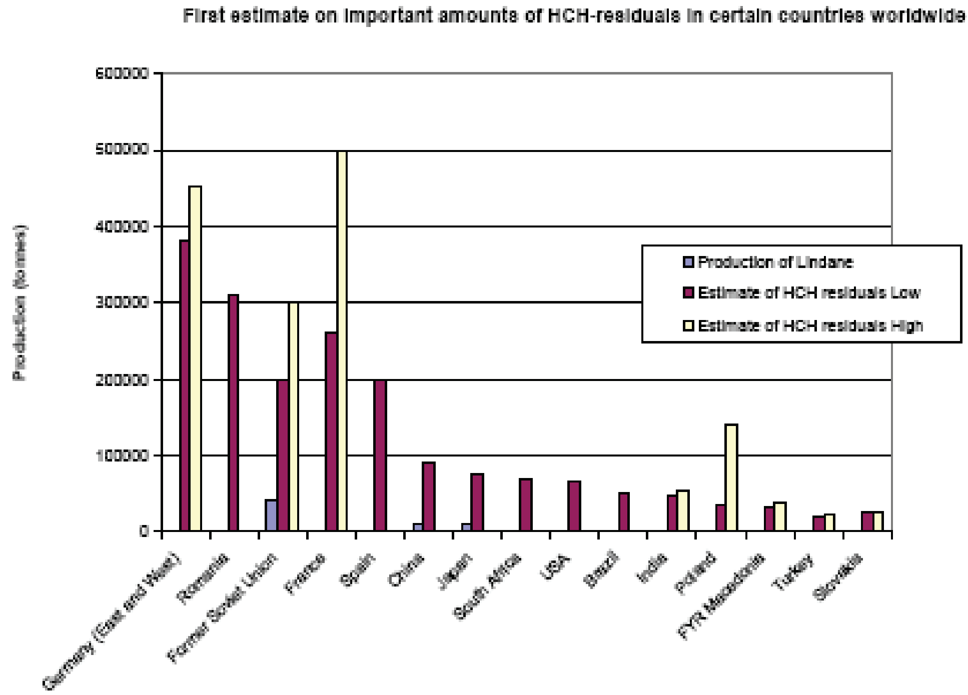

Figure 1: first overview of the main countries that own of HCH waste

Important is to remind that after the first production of technical HCH , which included a large amount of isomers that were useless for plant protection purposes, the more effective product lindane was produced based on the extraction of the gamma HCH, but this led to the generation of huge amounts of waste. This means that for each ton of Lindane between 8-12 tons of waste isomers (alpha, beta and delta) was produced.

Also the total estimated of HCH waste varies from 1.6 Million to 6 million tons
Two different approaches have been used sofar:

1. Find waste disposals + estimate tons HCH
This approach has been used by IHPA and gave a first indication of

- 1,6 – 1,9 Mio tons HCH
- But here new research and investigations will be included in the program

2. Search global Lindane use and multiply with 8 or 12 tons
This approach has been used by Li Fan Yi, (see ref 1 in Annex 1) lead to a total estimated use of Lindane 1950-2000:

- global Lindane use for agricultural use around 450 000 tons. Additional use of 150 000 tons of Lindane on livestock, forestry, human health and other purposes gave a total global use of 600 000 tons
- This lead to a minimum usage of 4,8 Mio tons (Factor 8) and a maximum use of 6 Mio tons

Continent	Usage (kt)	Percentage
Europe	287.16	63.32
Asia	73.20	16.14
America	63.57	14.02
Africa	28.54	6.29
Oceania	1.032	0.23
Total	435.50	100

Figure 2: Total Continental use as estimated by Yi Fan Lee in (Lit 1, in Annex IV: Global Lindane usage)

However both approaches have left a gap, in case of the minimum option of 3.2 million tons, and of 4.1 million tons in case of the maximum option and it is important that the inventory works will narrow this gap considerably.

Technological solutions

However as the stockpiles of HCH waste are often tremendous and can vary from several 10000s of tons till more than 100 000 tons, the implications on the materials produced by the treatment of HCH are even bigger. This gives large implications, by for example large amounts of salt produced, or as CaCl2, which have to disposed at special landfills, or in other cases if as HCl it could be supplied to chlorine industry, but then it will also affect their own supplies.

Some of the former Lindane producers had been applying at that time successfully applied conversion of the HCH waste to TCB, which could then be used for other purposes. However for TCB is now no use anymore and in most countries its use is forbidden. However the thought on re-use has become an important driver for this programme.

By addressing the treatment issue a large number of issues have to be looked into such as:

- Bad quality due to organics like Hg + heavy metals etc
- Amounts can be large in comparison to local HCl market (See also in Figure 3)
- High purity HCl needed and the need for purification of HCl from HCH will require extra costs
- Dumping huge amounts of HCl on local or regional markets can destroy balance between existing suppliers

Therefore next to the technological issues that have to be demonstrated, also a sustainable strategy to deal with these huge streams has to be developed in cooperation with the industry.

The issue on technologies is more complex as HCH mainly consists of 70% chlorine and therefore the treatment in common hazardous waste combustion plants, other than by strong dilution, is not quite sustainable. There are a number of specialised combustion plants that would be able to recycle HCl and also alternative non-combustion technologies would be able treat HCH and produce HCl and depending on the quality of the HCl this could be re-used by the chlorine industry.

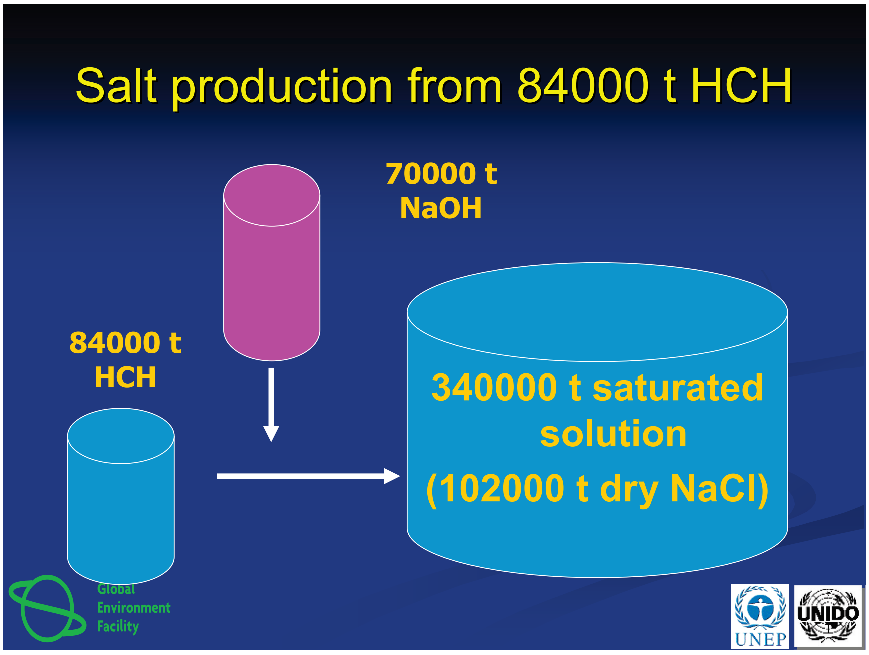

Figure 3: Example of a stockpile of 84000 tons and amounts of NaOH required and amounts of NaCl produced

Finally the re-use HCl by industry has to be technically investigated but also a global assessment of that capacity in the various continents will be implemented by the World Chlorine Council.

Summary:

- It is clear that the problem of HCH is complex and needs a global strategy before large HCH cases will be financed by the GEF
- The information is not sufficient and additional investigations have to be made on global amounts and at each location to assess volumes and its contents in relation to possible treatment
- Various technologies have to be tested on a number of HCH waste sites so the real problems and solutions can be assessed
- Quality criteria for the delivery of HCl from the HCH treatment have to be worked out in order to secure a smooth transfer to the production plants
- Global Capacity for HCl treatment/recycling has to be made
- Financial /Economical analysis of the whole cycle Removal-Treatment-transport to regional HCl recycling centres

References:

1. Vijgen John, The Legacy of Lindane HCH Isomer Production, January 2006, ISBN 87-991210-1-8

OBSOLETE PESTICIDES: A TICKING TIME BOMB AND WHY WE HAVE TO ACT NOW

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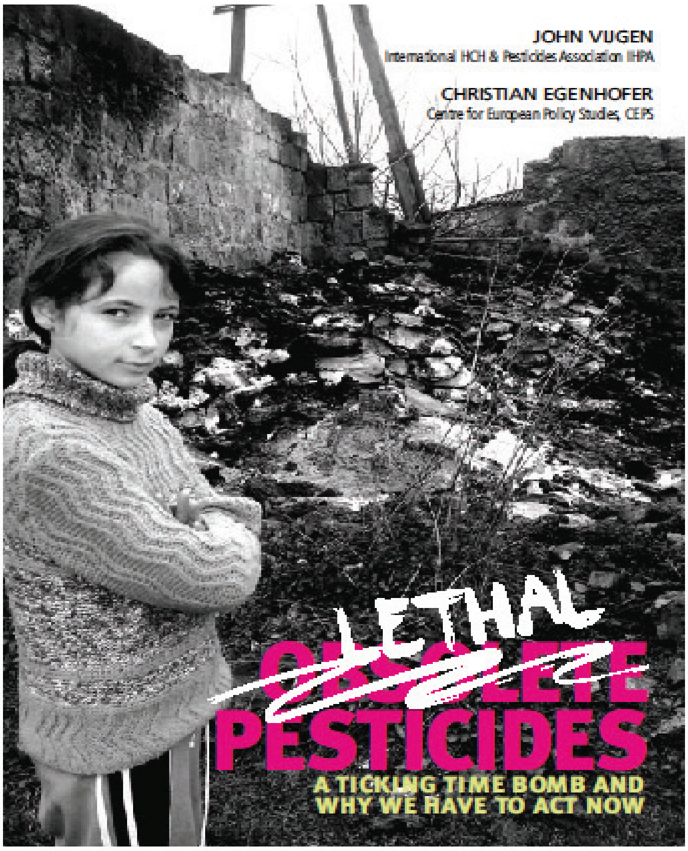


Introduction

The problem of obsolete pesticides has been addressed by the Stockholm Convention on Persistent Organic Pollutants (POPs). In the EU, producers have been legally obliged to manage obsolete pesticides (OPs), including organising their collection and destruction according to EU laws applicable to hazardous waste management. With EU enlargement, EU law has consequently become applicable to the new member states as well.
However, implementation of the provisions of the Stockholm Convention on their own is hardly sufficient to effectively deal with the risks associated with OPs. The Convention only deals with nine specific OPs (hereafter called Persistent Organic Pollutant or POP pesticides), which represent a small proportion of the total number that are obsolete. In addition, and in close geographical proximity to the EU, problems remain, **especially in South-East Europe and the countries of the former Soviet Union.**

There are considerable risks of not acting. Unprotected sites – estimated to number in the tens of thousands – constitute a lethal danger for humans and animals alike. OPs seriously risk undermining agricultural trade between the EU and non-EU countries from Europe and the former Soviet Union. The estimated direct and indirect damages as a result of the Nitrofen food scandal in Germany from 2002 alone have been estimated to exceed €500 million. OPs in non-EU countries also constitute an imminent risk for the EU because stocks are often stored near watercourses. OPs risk being washed into floodwaters especially in times of floods such as those in Germany in 2002 or in Romania, Ukraine and Moldova in 2008.
At the same time, the clean-up costs for OPs are relatively low, around €3,000 per tonne. With a total volume of an estimated 256,000 to 263,500 tonnes in the new EU member states, the accession countries, the countries of the European Neighbourhood Policy (ENP), the Russian Federation and Central Asia, the total required cost would be between some €770 and €790 million.
There are signs that some countries are willing to act. With the help of the World Bank, the Republic of Moldova has eliminated 1,150 tonnes of POP pesticides. In Ukraine, efforts are ongoing to export 1,000 tonnes of OPs to Germany for destruction and the elimination of a further 2,000 tonnes is already planned.
To further accelerate destruction, EU financial and technical assistance will be needed. At the same time, this will increase awareness, provide technical knowledge, generate domestic co-financing and in the medium term, possibly generate national legislation, where it is still missing.

Cases

A number of serious cases are briefly discussed:

Costs of inaction
In 2002, Germany and the EU were confronted with the consequences of the contamination of organic produce with Nitrofen in what was formerly East Germany. Food has been stored in a former pesticides storage building. Due to remaining contaminants in the soil of the storage facility, the stored food was contaminated. The German Farmers Association estimated in 2002 that direct and indirect damages due to the Nitrofen food scandal amounted to over €500 million.
Source: Brennpunkt LebenmittelSicherheit (2002).

Risks of inaction

The German Advisory Group on Economic Reform in 2002 wrote: "It is not unlikely that some agro-chemicals that have been banned for some time in the West continued to be used in the Soviet Union and later Ukraine. It is also safe to assume that some such chemicals were (are) less than ideal from a technical standpoint. Hence, it is not possible to reject out of hand the possibility of food contamination such as occurred with Nitrofen in Germany also occurring in Ukraine. Food industry insiders warn, in private, that a food safety time bomb is ticking in Ukraine."

Source: S. von Cramon-Taubadel (2002).

Ukraine is assumed to host nearly 13,000 sites that already are or potentially are contaminated with OPs. According to the Ukrainian authorities, total stocks amount to about 32,000 tons in 5,000 recognised sites. Many of the sites are freely accessible, posing a danger to trespassers and in particular to children and livestock grazing in the vicinity. Often, locations are in the countryside and therefore interface with agricultural production with residues leaching into the surrounding soil and groundwater, posing a threat to nearby water supplies.

Source: Antonov & Gamera (2007).

Ticking HCB time bomb in Kalush in Oblast Ivano-Frankisk in Western Ukraine

Along the banks of the Savka River, a tributary of the Dniester, which flows from Ukraine to Moldova, lies Europe's largest HCB stockpile. The Dniester River basin is home to more than 7 million people, and the river itself is the main source of drinking water in the Republic of Moldova and parts of Ukraine. The site is described as one of the national priority sites for treatment of POPs with the destruction of the burial site of 10,000 tonnes of HCB. It is estimated that this site alone contains about 30% of the total OP problem of Ukraine. The draft NIP (ready for official approval since 2006) proposes to destroy this stockpile. As the NIP is not approved, no action has been taken.

Sources: Environment and Security, 2007; UNECE, 2004; National Environmental Policy of Ukraine 2007; Antonov & Gamera, 2007; CLU-IN, 2008.

Elements for the way forward

There have been success stories of many countries catching up with their legacy and destroying OPs. This has been the case in the EU and other industrialised countries, including the new EU member states. In these countries, there is awareness, legislation, technical knowledge and funding. Some or all of these are missing in the ENP countries.

Yet even in this region, there is progress. The first regional project has been approved by the GEF Council. IHPA will start – on behalf of the FAO – to manage the GEF programme "Capacity Building on Obsolete and POPs Pesticides in Eastern European Caucasus and Central Asian (EECCA) countries" and will cooperate with the partners Milieukontakt International and Green Cross and the representatives of nine countries. The programme is to start at the end of 2009. The project comprises awareness-raising and capacity-building in the following nine countries: Albania, Armenia, Azerbaijan, Belarus, FYR Macedonia, Georgia, Republic of Moldova, Mongolia and Romania. It will attempt to strengthen regional cooperation and exchange of know-how and experiences by e.g. connecting countries and experts, and facilitating preparation and implementation of clean-up actions in any of the countries in the region.

At the same time, the FAO, backed by an UN mandate to manage OPs, is intending to publish a study on the problems of OPs in Central Asia and the Caucasus. The study results were presented at a workshop from 2–4 December 2008 in Baku, Azerbaijan. The host, the

Minister of Agriculture of Azerbaijan, underlined the seriousness of the situation and sent a strong appeal to take action now.
Other regional initiatives are currently being taken by the World Bank, which has recently initiated a Feasibility Study in Tajikistan, Kyrgyzstan and Uzbekistan (see also under 3.). In addition, the drawing up of a regional GEF project implemented by UNEP-WHO-Milieukontakt International and Green Cross for DDT covering the Caucasus and Central Asia should be mentioned. The DDT project deals with future breakouts of malaria cases in these regions and tries to identify ways of using alternatives and to destroy stockpiles of DDT. IHPA will in parallel with the GEF project continue to work on awareness-raising activities in the region, i.e. supporting individual initiatives such as MEP Wieslaw S. Kuc's travelling photo exhibition describing the situation at selected OP locations. But more is needed:

1. In order to achieve coverage in all the countries at the same time, it is proposed that the EU, possibly together with other donors, should finance more awareness-raising and capacity-building measures. Within the GEF, such a programme exists, but it would need to be expanded to cover all 30 and not only the present eight countries concerned: Albania, Armenia, Azerbaijan, Belarus, FYR Macedonia, Georgia, Republic of Moldova and Romania.

2. In parallel, on the political level, the EU should insist that those countries that have not yet done so should ratify the Stockholm Convention, namely Bosnia and Herzegovina, Montenegro, the Russian Federation, Serbia and Turkey.

3. A third step would be to build up reliable inventories. Inventories are the only sound basis for planning, budgeting and executing removal actions. Romania has started with an EU-funded programme to facilitate the preparation of inventories on a country-wide basis. Inventories, however, need capacity and capacity requires training. Training materials are already available at the FAO and other UN institutions, and a special training programme could be adapted for general use. The European Commission has profound experience with training programmes in the EU and non-EU countries. IHPA has assisted Romania in developing policies and strategies for preventing the emergence of new OP stocks. This is important work in the individual country and is ideally suited to being shaped in the same way as in the EU, where the 'return-to-sender' policy is imbedded in European and national legislation. The World Bank has initiated a Feasibility Study, which is now under implementation by the consortium Tauw, Witteveen + Bos, IHPA, Milieukontakt Int. and Green Cross on obsolete pesticides in Kyrgyzstan, Tajikistan and Uzbekistan, which deals with all aspects of inventory, risk assessment, feasibility of safeguarding, transport and elimination /disposal of OPs at three pilot sites plus a feasibility study of in-situ remediation and containment alternatives, based on training of locals for all components.

4. The most expensive part of OP clean-up is the removal of stocks for destruction or, if that is not possible, safeguarding. Currently, there is only support under the Stockholm Convention supplemented with incidental initiatives. Private financing on the other hand will depend on whether public financing will be available and notably whether reliable data on sites and inventories exist.

Proposal – Plan of Action

In order to solve the problems, there is a need for more awareness in countries that own OP stocks as well as countries that import food from countries with OP stocks. Further work on

better information on OP stocks by means of field inventories or possibly national studies is urgently needed. Moreover, there is a need to identify gaps in legislation, the establishment of Action Plans for elimination of OPs per country, measures to prevent future re-occurrence of OPs and the identification of funding needs.
We call for the European Commission to lead and develop an Action Plan in partnership with the EU member states, the European Parliament, non-EU countries such as those falling under the European Neighbourhood Policy and those in Central Asia, international organisations such as the FAO, UNEP, UNDP, UNIDO, World Bank and GEF, agricultural organisations, NGOs, consumer organisations and industry including chemical industry and food retailers. In particular, that Action Plan would call upon these institutions to take concrete action, as follows:

- The Council, led by the Presidency, would urgently address OPs in the Council Working Party on International Environment Issues.
- The European Parliament would:
  a. request an amendment of the pesticides strategy with binding requirements to report OPs stocks, and
  b. highlight OPs in the coming New Neighbourhood Strategy.
- The countries that still possess OPs would:
  a. make their removal a priority in their national environment plans,
  b. add their destruction to the agenda of negotiations with donors, while
  c. making national funds available for co-funding.
- The European Commission, the European Parliament and EU member states would improve the dialogue on the scale and urgency of the problem and possible solutions.
- New EU member countries would urgently comply with rules on reporting of OP stocks, quality of pesticides storage, etc.
- Plant protection associations (in cooperation with all national and international stakeholders) would design and ultimately establish so-called ‘empty container programmes’ to collect and destroy OPs along the lines of recent efforts made in France or Poland

The complete book can be downloaded at http://www.ihpa.info/resources/library under
II. IHPA REPORTS
Obsolete (lethal) Pesticides, a ticking time bomb and why we have to act now.

CAPACITY BUILDING ON OBSOLETE AND POPS PESTICIDES IN EASTERN EUROPEAN CAUCASUS AND CENTRAL ASIAN (EECCA) COUNTRIES

Mark Davis[1], Sandra Molenkamp[2], Stephan Robinson[3], Vladimir Shevtsov[4], John Vijgen[5]
FAO[1], Milieukontakt International[2], Green Cross Switzerland[3], Green Cross Belarus[4], International Hexaclorocyclohexane (HCH) and Pesticides Association (IHPA)[5]

What is the problem?

Mismanagement and accumulation of obsolete pesticides and POPs pose a threat to health and environment locally, regionally and globally. It is very difficult to assess the real extent of the obsolete pesticides problem as only a limited number of field investigations have been carried out. However, it is estimated that **over 500 000 tonnes of OPs and POPs contaminate the environment worldwide.**
Obsolete pesticides (OPs) are found mainly in three forms:
1. Stocks in and around former storages (spread over tens of thousands of locations) varying from several kilos to tens or hundreds of tonnes;
2. Stocks at collection points in the former Soviet Union, the so-called polygons or burial sites. These are special landfills designed for the controlled storage of outdated pesticides and other hazardous waste. Polygons - in the sheer nature of the concept - comprise a limited number of very large sites, often in combination with other hazardous waste;
3. Waste originating from the production of pesticides; the main component is HCH (hexachlorocyclohexane) waste stemming from the production of Lindane. HCH waste is distributed on a limited number of sites with large amounts of waste up to sometimes more than hundred(s) thousands of tons.
Article 6 of the Stockholm Convention requires countries party to the Convention to take measures to eliminate or reduce the release of OPs and POPs into the environment.

How to deal with the problem?

The project **Capacity Building on Obsolete and POPs Pesticides in Eastern European Caucasus and Central Asian countries** will support 9 countries to implement such measures.

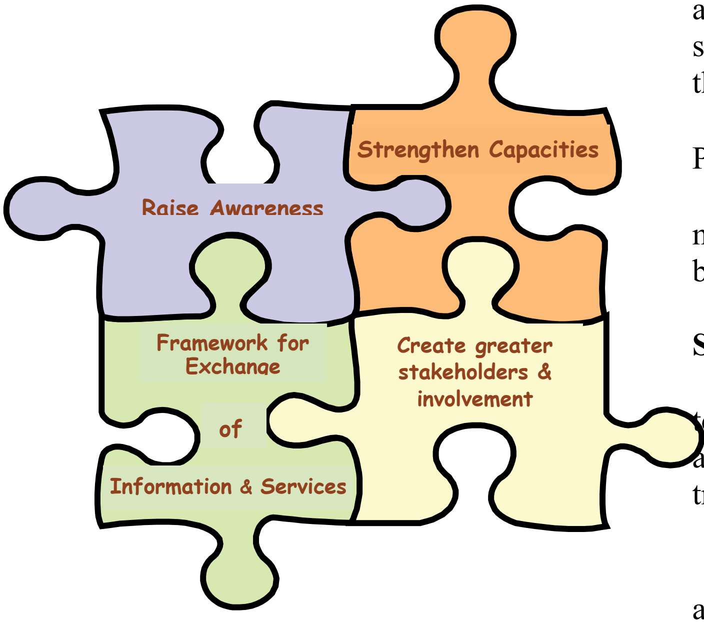
This regional initiative includes 9 countries (Albania, Armenia, Azerbaijan, Belarus, Georgia, Mongolia, Republic of Moldova, Romania, The Former Yugoslav Republic of Macedonia) will start up this month this GEF project and will run over 3 years from September 2009 till December 2011. The inception workshop will take place from 22 till 25 September in Tirana, Albania.

In September 2009 GEF, FAO, Green Cross, IHPA and Milieukontakt International have started this new project. The aim is to create a strong platform on the elimination of obsolete pesticides and POPs in 9 countries of Eastern Europe, Caucasus and Central Asia.

The final result will bring a greater awareness of the danger of obsolete pesticides and an increased capacity to manage, dispose of and prevent obsolete pesticides and

POPs stockpiles. In addition, the project will bring about information exchange and cooperation between 9 participating countries, as well as stimulate a systematic involvement of a wide range of stakeholders.

The following activities planned within this project can be seen from the schedule:



Raise Awareness:

Participation at 10^{th} & 11^{th} Int. HCH and Pesticides Forum (2009 +2011) with a special workshop on Central Asia during the 10^{th} Forum (with support of FAO)

Production & dissemination of project PR materials

Participation at relevant (international) meetings: presentations, exhibitions and brochure distribution

Strengthen Capacity:

Workshops & Training Sessions related to Obsolete pesticides management (such as inventory of OP stocks and repacking trainings)

Technical & Legal Guidance materials

Portfolio of destruction technologies and management options for the participating countries

Establishment of a Framework for Exchange of Information & Experiences:

- Commonly Agreed Information Exchange Mechanism
- Dissemination results
- Other info: interactive website, CDs, videos, printed materials

Enlarge and Improve Stakeholder Involvement:

- Regional Capacity Needs Analysis Study
- Stakeholder partnerships

<table>
<tr><td></td><td>Field Works include:
Safeguarding of at least one high risk Obsolete/POPs Pesticides stock
Securing storage in 3 countries
Management Plans in 3-5 countries
Training 2 Trainers per country on Management of Obsolete and POPs pesticides</td></tr>
<tr><td>Group Training on Safety in the field</td><td></td></tr>
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Finally, the project aims to create a Platform for Obsolete and POPs Pesticides Elimination and Prevention in Eastern European Caucasus and Central Asian (EECCA) countries

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Section 2: POPs management in the Czech Republic – experiences, …

CZECH REPUBLIC - INVENTORY OF SITES CONTAMINATED WITH PERSISTENT ORGANIC POLLUTANTS

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1. INTERNATIONAL AND EUROPEAN COMMITMENTS

The Czech Republic is the party to the Stockholm Convention on Persistent Organic Pollutants (POPs) and the member state of the European Union. The Stockholm Convention on POPs was adopted on 22 May 2001 and is, among other Conventions, the international environmental agreement recognising that POPs possess toxic properties, resist degradation, bioaccumulate and are transported, through air, water and migratory species, across international boundaries and deposited far from their place of release, where they accumulate in terrestrial and aquatic ecosystems [1]. The Czech Republic is fully aware of the health solicitudes resulting from local exposure to POPs, in particular impacts upon women and, through them, upon future generations.

The European Community and its member states are seriously concerned by the continuous release of POPs into the environment. Further measures need therefore to be taken in order to protect human health and the environment against these pollutants. In order to ensure coherent and effective implementation of the Community's obligations under the Convention, it was necessary to establish a common legal framework, within which to take measures designed in particular to eliminate the production, placing on the market and use of intentionally produced POPs. Obsolete or carelessly managed stockpiles of POPs and the importance of identifying and separating waste consisting of, containing or contaminated by POPs at source as well as the needs for establishment of the necessary measures resulted into the adoption of the Regulation (EC) No. 850/2004 of the European Parliament and of the Council of 29 April 2004 on persistent organic pollutants and amending Directive 79/117/EEC [2]. Concentration limits of substances subject to waste management provisions set out in article 7, minimum and maximum concentration limits are set in amendments to the Regulation. Further disposal and recovery operations ensuring that the POPs content is destroyed or irreversibly transformed are permitted including pre-treatment, repackaging and temporary storage operations.

Since 29 April 2004 up to now the Regulation has been six times amended due to the scientific and technical progress and changed from the reporting and legislative reasons. The text of the Regulation with its supplements is available here: http://europa.eu/scadplus/leg/en/lvb/l21279.htm

The Czech legislative system implemented the Regulation on POPs through the Act on Waste No. 185/2001 Coll. and as its amendment No. 34/2008 Coll. from 16 January 2008 [3]. Reference to the Regulation, definition of wastes consisting of, containing or contaminated by POPs, the authorisation for inspection of the Czech Environmental Inspectorate and the list of substances subject to waste management were set newly in the Act on Waste.

2. CZECH NATIONAL OBLIGATIONS AND TARGETS

The updated State Environmental Policy of the Czech Republic (SEP CR) is conceived so as to define a consensual framework for long-term and medium-term directing of the development of the environmental dimension of sustainable development in the CR [4]. SEP CR is a response to incentives following from the results of the evaluation of implementation of the previous SEP CR and it respects the responsibilities and obligations that result from the membership of the CR in the EU, UN and OECD. SEP CR is a document which strengthens and improves partner cooperation with other sectors – corresponding to the principles of sustainable development. This document also offers a range of instruments for achieving the set targets - regulatory, economic, informational, voluntary etc.

The Environmental Damage Department of the Ministry of the Environment is responsible body for the contaminated sites management, prevention and remedying environmental damage from the past and environmental liability set in the Act No. 167/2008 Coll. [5].

Contaminated site means any soil, land, rock formation, building constructions, surface or groundwater contamination caused by the inappropriate or illegal management of hazardous wastes and/or chemicals, e.g. petroleum products, pesticides, PCBs, chlorinated and polyaromatic hydrocarbons, heavy metals etc. Old/historical contaminated sites (ecological or environmental burdens/loads/damage) are those where either the polluter is unknown or polluter does not exist any more. Unauthorized landfills, abandoned industrial places, agricultural factories and facilities, unprotected storage of hazardous wastes and chemicals, former military bases or any extracting, mining and quarrying mines areas might be considered as a contaminated site as well (http://www.mzp.cz/en/contaminated_sites).

The National Implementation Plan for Implementation of the Stockholm Convention (NIP) of the Czech Republic [6] was worked out according to the Guidance for developing national implementation plans for the Stockholm Convention. The NIP was tailored to define the needs of the Czech Republic to meet the obligations of the Convention by:

- Giving basic background information on POPs situation in the country;
- Describing the phases of the NIP development process;
- Giving guidance on the objectives of each phase, the outcomes, the tasks to be undertaken and the method applied;
- Summarizing available guidance material which may be useful; and
- Setting short and long term targets in the field of POPs contaminated sites management, prevention and remedying environmental POPs damage.

3. PROJECT ON THE INVENTORY OF POPs CONTAMINATED SITES IN THE CZECH REPUBLIC

The NIP's [6] strategic goal 3.8.1 "Identification and environmentally sound management of contaminated sites" started up the Project on the inventory of POPs contaminated sites in the Czech Republic (POPs Project). The Project outcomes will be a partial phase of the National Inventory of Contaminated Sites (Národní Inventarizace Kontaminovaných Míst – NIKM) in the Czech Republic. NIKM is divided into 2 parts which have to update and collect data on contamination of different polluted or potentially polluted sites. The importance of one-approach gleaning, mapping, new site identification, evaluation and interpretation of contamination has been identified within the Ministry's priorities. Secondly the future implementation of a Directive establishing a framework for the protection of soil [7] currently discussed in the European Union will be the obligation of the country as the member state of the EU. The draft of the Directive sets, among others, measures for the Identification and inventory of contaminated sites and Remediation strategy.

The main aim of the two years POPs Project started in September 2008 is to compile basic data on existing contaminated sites and locations potentially consisting of, containing or contaminated with certain POPs chemicals and pesticides listed in the Convention [1], in the Regulation [2] and in the Act on Waste [3].

List of substances subject to POPs Project and waste management provisions of the Act on Waste [3] and Regulation [2].

Substance	CAS No.	EC No.
Aldrin	309-00-2	206-215-8
Chlordane	57-74-9	200-349-0
Dieldrin	60-57-1	200-484-5
Endrin	72-20-8	200-775-7
Heptachlor	76-44-8	200-962-3
Hexachlorobenzene (HCB)	118-74-1	200-273-9
Mirex	2385-85-5	219-196-6
Toxaphene	8001-35-2	232-283-3
Polychlorinated Biphenyls (PCBs)	1336-36-3 and others	215-648-1 and others
DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane)	50-29-3	200-024-3
Chlordecone	143-50-0	205-601-3
Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs)		
Hexachlorocyclohexane (HCH), including Lindane	608-73-1, 58-89-9	210-168-9, 200-401-2
Hexabromobiphenyl (HBB)	36355-01-8	252-994-2

Data obtained will subsequently become the part of the Contaminated Sites Database System - Systém evidence kontaminovaných míst (SEKM) - as well as the priority and the risk profile of each contaminated site shall be evaluated.

POPs Project, its first step, is mainly about the data collection, the asking questions and the spending a time in the specific potentially contaminated locations with POPs. No waste or soil sampling and laboratory analyses will be carried out within the years 2008 and 2009.

The company RMT VZ, a.s. Praha, Czech Republic, was chosen for the POPs Project in the open public tender in August 2008. Twelve companies were invited to send to the Ministry the proposal on how to proceed and manage the inventory of contaminated sites with POPs in the country. The maximum limited proposed cost of the tender was 2,000,000 CZK without 19%-tax (approx. 74,700 EUR plus 19%-tax) from the budget of the Environmental Damage Department of the Ministry of the Environment. The contract was signed at the beginning of November 2008.

The joint-stock company RMT VZ, a.s. Praha has prepared the full project proposal containing step-by-step procedures, the content of the POPs Project and its schedule. The subjects of the POPs Project are only the substances shown in Table above. No specific concentration limit on contaminated site was given. It means that any site contaminated with one or more substances (in the Table above) and with concentration higher than zero is included in the POPs Project if known or put on the list by various sources in the country:

- Competent regional and local authorities;
- the Czech Environmental Inspectorate;
- the National Implementation Plan for Implementation of the Stockholm Convention;

- NGOs and local citizens;
- the Contaminated Sites Database System - Systém evidence kontaminovaných míst (SEKM);
- the Ministry of Agriculture and the Ministry of Defence of the Czech Republic; and
- the biggest private companies in the Czech Republic.

The POPs Project excluded from its focus following sites or companies:

- Officially authorized facilities handling both non-hazardous and/or hazardous wastes;
- Incineration plants currently in operation;
- Landfills sites currently in operation;
- Authorized storages of both non-hazardous and/or hazardous wastes;
- Companies, holders and operators of PCBs wastes and PCBs containing equipment;
- Locations where transformers or energy transform stations are situated; and
- Sites containing polyaromatic hydrocarbons.

As of 8 June 2009, 851 contaminated and potentially contaminated sites with POPs were indicated and additional 130 tarmacadam plants were included into the POPs Project. The contaminated sites are formed:

- 30 % former municipal landfills sites;
- 25 % of sites proposed by the Ministry of Agriculture as pesticides contaminated;
- 23 % of industrial or enterprise areas, mostly abandoned;
- 8 % electro energy supplying companies;
- 4 % already closed industrial landfills;
- < 4 % - military areas, mines, petroleum refining, natural gas purification and pyrolytic treatment of coal areas, and other contaminated sites.

Luckily, neither open-air pesticides stockpiles nor abandon POPs waste storages were found yet.

The overall number of the POPs potentially contaminated and POPs contaminated sites in the Czech Republic will be known and available in December 2009/January 2010. The Environmental Damage Department expects the follow-up POPs Project public tender in spring 2010.

4. REFERENCES

[1] Stockholm Convention on Persistent Organic Pollutants
[2] Regulation (EC) No. 850/2004 of the European Parliament and of the Council of 29 April 2004 on Persistent Organic Pollutants and amending Directive 79/117/EEC
[3] Act No. 185/2001 Coll., on Waste and its Amendments which came in force in May 15th 2001
[4] Updated State Environmental Policy of the Czech Republic from 2004 – 2010
[5] Act No. 167/2008 Coll. on prevention and remedying environmental damage and amendment on some laws
[6] Government Decision No. 1572/2005 of 7 December 2005 on the National Implementation Plan for Implementation of the Stockholm Convention in the Czech Republic
[7] Czech Presidency Proposal for a Directive of the European Parliament and of the Council establishing a framework for the protection of soil of 19 May 2009

EUROPEAN UNION PESTICIDES REGULATION SYSTEM - APPROACH DEVELOPMENT

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Provisions, conditions and procedures for the authorization, placing on the market, use and control of pesticides in the commercial form of plant protection products within the European Community were subject of national approach in the past. There was identified the need for harmonization of the provisions laid down in the European Union (EU) Member States towards application of uniform rules on the conditions and procedures by all EU Member States. Thus, having regard to the Treaty establishing the European Economic Community (EEC), and in particular Article 43 thereof, the Council of the European Communities has adopted the Council Directive 91/414/EEC of 15 July 1991, concerning the placing of plant protection products on the market [1]. Member States implemented the Directive 91/414/EEC within two years in the form of national laws, regulations and administrative provisions necessary to comply with the provisions of this Directive. One of the most important parts contained in the Article 4 of the Directive 91/414/EEC were the provisions on the review of all existing active substances based on the evaluation of all their properties on the EU level. This work, excluding few compounds, was finalized on the 31 December 2008. Based on the experiences gained within 15 years of the EU review process there was few years ago started drafting of a new EU Regulation replacing Directive 91/414/EEC. It is expected that this EU Regulation, containing some new provisions related to better environment protection will be approved this year and will be in force at the beginning of 2011.

Key words: pesticides, plant protection products, placing on the market, pesticides regulation, Directive 91/414/EEC, existing active substance, new active substance, EU active substances review process, uniform principles, risk assessment, risk management

Human health and the environment is a major concern for European Commission policy on the authorisation of plant protection products containing pesticide active substances.

In the European Union, no plant protection product can be used unless it has first been scientifically established that:

- they have no harmful effects on consumers, farmers and local residents and passers-by;
- they do not cause unacceptable effects on the environment;
- they are sufficiently effective against pests.

As to the European Union (EU) membership status there are currently twenty seven EU Member States and three Candidate Countries.

EU Member States are Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania,

Luxemburg, Malta, Netherlands, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden and United Kingdom.
Candidate Countries are currently Croatia, Former Yugoslav Republic of Macedonia (FYROM) and Turkey.

There can be in principle identified three basic historical periods of the EU pesticides regulation system approach development as to the influence of pesticides on the human health and the environment:

1) Before Council Directive 91/414/EEC
2) Council Directive 91/414/EEC in force
3) Regulation of the European Parliament and of the Council of the European Union replacing Council Directive 91/414/EEC

<u>1) Before Council Directive 91/414/EEC:</u>

In this period provisions, conditions and procedures for the authorization, placing on the market, use and control of pesticides in the commercial form of the plant protection products within the European Community were subject of national approach in certain member states.
There were different systems used in different EU Member States as to the data requirements, data evaluation models and risk mittigation measures based on the evaluation results. The most sophisticated systems of pesticides regulation were developed and used e.g. in United Kingdom, Germany and Netherlands.
In general there was lack of data especially on the environment fate and behaviour of the pesticide active substances and effects on some non-target organisms.
Based on the development of the European Community free market of goods there was need for harmonization of the provisions laid down in different EU Member States towards application of uniform rules on the conditions and procedures for pesticides regulation (risk assessment and risk management) by all EU Member States.

<u>2) Council Directive 91/414/EEC in force:</u>

To fulfill the requirements on the harmonised system for pesticides and formulated plant protection products there was developed and approved regulatory procedure under the Council Directive 91/414/EEC. Within this Directive and a set of amending Directives there were laid down harmonized requirements on data, risk assessment and risk management criteria for 'existing' (i.e. being on the market in EU Member States before the Council Directive 91/414/EEC being in force) and 'new' active substances.
Basic provisions to launch the review procedure on evaluation of the properties of 'existing' active substances were laid down by this Directive.
Each active substance has to be proven safe in terms of human health, including residues in the food chain, animal health and the environment, before being allowed to be placed on the market in the form of plant protection product.
All active substances (both 'existing' and 'new') are approved on the EU level, whilst plant protection products are authorised on the EU Member States level. EU Member States may

authorise only plant protection products containing approved active substances.

There are altogether six Annexes to the Directive 91/414/EEC:
- Annex I - list of included active substances ('positive list' of approved active substances)
- Annexes II and III - data requirements for active substances (Ann.II) and products (Ann.III)
- Annex IV and V - list of 'risk' (Ann.IV) and 'safety' (Ann.V) phrases
- Annex VI - 'Uniform Principles' for data evaluation (risk assessment and risk management)

Detailed data requirements on the active substances and plant protection products are laid down in the amending Directives to the Directive 91/414/EEC, namely Directives:
- 94/37/EC (identity of the active substance)
- 93/71/EEC (efficacy and official recognition of efficacy trials)
- 94/79/EC (human toxicology and metabolism)
- 95/35/EC (analytical methods)
- 95/36/EC (fate and behaviour in the environment)
- 96/12/EC (ecotoxicology)
- 96/46/EC (analytical methods)
- 96/68/EC (residues in or on treated products, food and feed)
- 97/57/EC (establishing Annex VI to the Directive 91/414/EEC ‚Uniform Principles' for evaluation and authorisation of plant protection products based on risk assessment and risk management)
- 2001/36/EC (micro-organisms and viruses)

Guidelines for data (dossier) submission by industry and review reports by EU member states:

(a) until 31st December 2005:

- Document 1663/VI/94 Rev 8 (Guidelines and Criteria for the Preparation and Presentation of Complete Dossiers and of Summary Dossiers for the inclusion of Active Substance in Annex I of Directive 91/414/EEC)
- Document 1654/VI/94 Rev 7 (Guidelines and Criteria for the Evaluation of Dossiers and for the Preparation of Reports to the European Commission by Rapporteur Member States Relating to the Proposed Inclusion of Active Substances in Annex I of Directive 91/414/EEC)

(b) since 1st January 2006:

- OECD Guidance for Industry Data Submissions on Plant Protection Products and their Active Substances (Dossier Guidance), *Re 2*, OECD Environment Directorate, May 2005
  (Guidelines and Criteria for Industry for the Preparation and Presentation of Complete Dossiers and of Summary Dossiers for Plant Protection Products and their Active Substances in Support of Regulatory Decisions in OECD Countries)
- OECD Guidance for Country Data Review Reports on Plant Protection Products and their Active Substances (Monograph Guidance), *Rev 2*, OECD Environment Directorate, May 2005
  (Guidelines and Criteria for the Evaluation of Dossiers and for the Preparation of Reports by Regulatory Authorities in OECD Countries Relating to the Evaluation of Active Substances, the Registration of Plant Protection Products and the Establishment of Maximum Residue Limits (MRLs) and Import tolerance)

Existing Active Substances‘ Review Regulations:

Stage Number (List Number)	Regulation Number	Number of existing active substances to be reviewed
stage 1 (1st list)	Regulation 3600/92	90 active substances
stage 2 (2nd list)	Regulation 451/2000	149 active substances
stage 3 (3rd list)	Regulation 451/2000	402 active substances
stage 4 (4th list)	Regulation 1112/2002 and Regulation 2229/2004 (including 10 new MSs)	193 & 50 ‚existing/new‘ active substances

Some active substances contained in the plant protection products were non-defended by industry and thus plant protection products containing them were withdrawn from the market (see e.g. Commission Decisions of July 2003, January 2004, June 2007).

As to the inclusion/non-inclusion of the active substances in Annex I to the Directive 91/414/EEC there were issued:
- Directives on inclusion of ‘existing’ and ‘new’ active substances in Annex I
- Decisions on non-inclusion of ‘existing’ and ‘new’ active substances in Annex I

3) Regulation replacing Directive 91/414/EEC:

Some important objectives of the Regulation proposal:
- better protection of human health, animal health and the environment (e.g. to eliminate use of endocrine disruptors)
- to provide harmonised rules on the placing of the plant protection products on the common market
- to speed up decision making

New provisions laid down on evaluation of certain properties of another compounds than active substances contained in the commercial plant protection products (synergists, safeners, co-formulants, adjuvants).

Drafted new definitions and legal instruments for:
- criteria for approval of active substance, safener or synergist (not considered to be a POP – Persistant Organic Pollutant, or PBT - Persistent, Bioaccumulative and Toxic substance, or vPvB – Very Persistent and Very Bioaccumulative Substance)
- comparative assesment of different active substance properties for similar use
- substitution principle of more toxic active substance by safer lower risk substances
- zonal mutual recognition (obligatory in three EU zones + greenhouse and post-harvest uses all around the three EU zones)
- minor uses / minor crops
- parallel trade of plant protection products (plant protection product registered in both EU Member States - country of export and country of import)

Annexes to the proposed Regulation replacing Directive 91/414/EEC:

- Annex I - definition of EU zones for the authorisation of plant protection products (PPPs)
- Annex II - procedure and criteria for the approval of active substances, safeners and synergists
- Annex III - list of co-formulants which are not accepted for inclusion in PPPs
- Annex IV - comparative assessment of PPPs containing candidates for substitution
- Annex V - repealed Directives (91/414/EEC, 79/117/EEC) and their successive amendments

State of affairs and dates foreseen for the proposed Regulation approval:
- EU Commission proposal on 19 July 2006
- First reading in the European Parliament (EP) on 23 October 2007
- Political agreement on 23 June 2008 in the Council of EU
- Common position on 15 September 2008
- ENVI Committee voted on 5 November 2008
- EP plenary to vote in December 2008 or January 2009; finally to vote in June 2009 (failled); expected to vote in September 2009
- Entry into force in the EU Member States after 18 months – expected February/March 2011

New potential sources for new obsolete pesticides stocks creation:

- illegal import of generic plant protection products from non-EU states
- illegal import of generic pesticide active ingredients for manufacturing of commercial formulations of plant protection products in EU Member States

? parallel import of plant protection products approved in EU Member States - Article 52 Parallel trade of the Draft Regulation replacing Directive 91/414/EEC - parallel import of the plant protection product into one European Union Member State is an import of the plant protection product authorised in the exporting EU Member State, which is identical in composition to the product already authorised in the importing EU Member State (reference product).

Important information available on the European Commission (DG SANCO) Website:

(a) For Plant Protection - Evaluation & Authorisation:
http://ec.europa.eu/food/plant/protection/evaluation/index_en.htm

(b) For Active Substances EU Status:
http://ec.europa.eu/sanco_pesticides/public/index.cfm

(c) For EU MSs/EC/EFSA Contact Points:
http://ec.europa.eu/food/plant/protection/evaluation/contact_points_rev47.xls

(d) For European Food Safety Authority (EFSA):
http://www.efsa.europa.eu/EFSA/efsa_locale 1178620753812_home.htm

References:

[1] Council Directive 91/414/EEC of 15 July 1991 concerning the placing of plant protection products on the market (OJ No L 230, 19.8.1991, p. 1.)

CONNECTIONS BETWEEN HCH AND SOME OTHER PESTICIDES IN THE FORMER CZECHOSLOVAK CHEMICAL PRODUCTION

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Abstract
Czechoslovak production of hexachlorocyclohexane (HCH) and related pesticides is briefly portrayed. It started in the early 1950s in the former Dynamit Nobel, then Chemical Works J. Dimitrov (now Istrochem) in Bratislava, later (1961) also in Spolana Neratovice. From all 5 stereoisomers, the most effective gama-HCH (Lindane) was isolated. In 1965, Spolana introduced complex treatment of remaining ballast stereoisomers with the final goal to produce tetrachlorobenzene (TCB) and hexachlorobenzene (HCB). The latter was used as the active component of combined fungicidal preparation (*AGRONAL H*), designated to dry treatment of seed. A part of HCB was transformed to sodium pentachlorophenolate and then to pentachlorophenol (PCP). PCP served as the effective principle of a combined insecticidal and fungicidal formulation (*PENTALIDOL*), designated against wood-eating pests (later innovated as *NEOPENTALIDOL*). Tetrachlorobenzene (TCB) was used for manufacturing sodium 2,4,5-trichlorophenolate. This was initial product for sodium 2,4,5-trichlorophenoxy acetate (2,4,5-T) and through esterification for the final product - butyl ester of 2,4,5-T that was the main component of arboricides, depicted as *ARBORICID E 50* and *ARBORICID EC 50.* Similarly like at all worldwide producers using this procedure, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) was formed through parallel condensation of two molecules of sodium 2,4,5-trichlorophenolate at higher temperatures with later known consequences, leading to closure of the production site in April 1968. The author was the first to analyse 2,4,5-T butyl ester from the production site (1974) and to perform the first on-site toxicological assessment suggesting the mood of clean-up of inner surfaces and destruction of equipment (1974-76).

Keywords
HCH, lindane, tetrachlorobenzene, hexachlorobenzene, pentachlorophenol, fungicides, trichlorophenolate, 2,4,5-T, arboricides, TCDD.

Introduction
Based on the history and author´s personal experience and engagement, this paper reveals the connections among some chlorinated pesticides (starting with DDT and HCH) manufactured since the early 1950s subsequently in two enterprises of the Czechoslovak chemical industry located in Bratislava (Slovakia) and Neratovice (Bohemia). To avoid some frequent misunderstandings, it is suitable to note that the crude HCH was then usually depicted also as benzene hexachloride (BHC) due to the method of synthesis (not to take by mistake for hexachlorobenzene – HCB) As for the HCH concerned, while the original producer in Bratislava only was limited to HCH and its most potent isomer Lindane, the production at the second one in Neratovice was marked beside Lindane with a broader spectrum of chlorinated pesticides derived from treatment of ballast HCH isomers, leading to tetrachlorobenzene (TCB) and mainly

hexachlorobenzene (HCB) utilised in the first line as active component of a fungicidal preparation, secondly for manufacturing pentachlorophenol, utilised as an active component of mixed insecticidal and fungicidal formulations against wood-eating insects. Tetrachlorobenzene (TCB) was initial product for manufacturing sodium salt of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). The respective butyl ester was the active component of herbicidal formulations with defoliation effects used in agrochemical practice as powerful arboricide. Similarly like at other producers manufacturing 2,4,5-T via condensation of 2,4,5-trichlorophenolate with chloroacetic acid (e.g. Philips-Duphar/NL, Boehringer/D, Solvay/D, Eastman Kodak/US, Union Carbide/US, Monsanto/US, ICI/GB, Hofmann-La Roche/CH and like) some unpleasant effects had occurred at workers (skin lesions like *acne chloria, porphyria cutanea tarda)* in the 2^{nd} half of the 1960s. This was the first manifestation of undesired by-product, TCDD, created through parallel condensation of two molecules of sodium 2,4,5-trichlorophenolate. Based mainly on the information by Boehringer, confirmed by medical investigation of employees (in the first time only dermatological), the facility manufacturing polychlorophenols and herbicides on the 2,4,5-T basis was closed in April 1968 and any access was strictly prohibited. This facility was subject of analytical and toxicological investigation by the author (1974-1976) leading to the first proposals on decontamination and to further negotiations on various levels (lasting for nearly four decades) on the final decontamination of the said facility and its total destruction by razing.

Commencement of the Czechoslovak production of chlorinated pesticides in Bratislava

For the first producer of chlorinated pesticides in Czechoslovakia, starting with DDT since the early 1950s, the Czechoslovak Planning Commission and Ministry of Chemical Industry selected former factory of heavy chemical industry known for a long time as *Dynamit Nobel* Bratislava, then *Chemical Works J. Dimitrov (CHZJD)* now *ISTROCHEM,* belonging then to the industrial group *Slovchémia* Bratislava. The reason was not only to increase the technological level of Slovak industry to enhance it on the level of Czech industry but at the same time to exploit efforts of the Research Institute of Agrochemical Technology (VÚAgT) constituted already in the late 1940s. In this institute subordinated to the Czechoslovak Ministry of Chemical Industry, excellent creative group in synthetic organic chemistry, organic technology and process engineering was formed, able to introduce a remarkable series of new productions into technological practice. This group, headed by R. Smrž (excellent organic and physical chemist educated at University of Vienna, by the way the author´s tutor in 1954-57) was further represented by V. Tichý (talented organic chemist, working for a long time in France) and J. Auerhan (responsible for process engineering). This collective was decorated by the State Prize in the mid-1950s for introducing about 19 production lines on various scale for a couple of special chemicals, among them DDT, HCH, Lindane and several other chemicals that were short on the Czechoslovak chemical market. It is perhaps suitable to note that the demand on then chlorinated pesticides was very high also due to the Korean War (1950-53) where reportedly biological weapons were used, so that the first batches were manufactured on the pilot plant equipment installed in VÚAgT before starting the full scale production in CHZJD. The orientation of this institute and of the factory to agrochemistry was stressed by parallel research, development and production of basic organophosphorus insecticides by another creative group represented beside R. Smrž and V. Tichý mainly by Š. Truchlík, J. Drábek, Š. Kováč, Š. Bátora and J. Bečka. The method of treatment of ballast isomers of HCH that were used later for manufacturing other pesticides at the second producer stems from this institute.

Hexachlorocyklohexane and other pesticides at the second producer

Steadily increasing domestic demand mainly promoted by the socio-political requirement on self-dependence of socialist Czechoslovakia on cereals and cheap food products as well as growing export of agrochemicals have led to decision to introduce the second production site for pesticides. From two industrial groups (*Chemopetrol* Prague and *Unichem* Pardubice) governing the chemical industry in Bohemia and Moravia, young growing factory *Spolana* Neratovice (subordinated to *Chemopetrol*) was selected to be oriented *inter alia* to agrochemistry.

The production of hexachlorocyclohexane (HCH) in *Spolana* Neratovice commenced in 1961. From the mixture of all 5 stereoisomers and higher-chlorinated products, the most effective isomer, i.e. gama-HCH (Lindan) was isolated. In 1965, the complex utilisation of ballast isomers through dehydrochlorination to trichlorobenzene that was further treated with oriented chlorination to the mixture of tetrachlorobenzene (TCB) and hexachlorobenzene (HCB).

Hexachlorobenzene (HCB) was used for manufacturing combined fungicidal preparation to dry treatment of seed (AGRONAL H), containing 10 % HCB and 2 % Hg in the form of phenylmercurichloride. A Part of HCB was treated with sodium hydroxide to sodium pentachlorophenolate and then to pentachlorophenol (PCP).

Pentachlorophenol (PCP) was used as the active component in a preparation with combined insecticidal and fungicidal effects PENTALIDOL, designated against food-eating pests (5 % PCP, 2 % DDT, 1 % Lindane), later, in the innovated formulation without DDT, depicted as NEOPENTALIDOL (5 % PCP, 2 % Lindane).

Tetrachlorobenzene (TCB) was transformed to sodium 2,4,5-trichlorophenolate. This compound was the initial raw material for manufacturing sodium salt of 2,4,5-trichlorophenoxy acid (2,4,5-T) through condensation with trichloroacetic acid. Esterification of this salt with butyl alcohol yielded the final product – butyl ester of 2,4,5-trichlorophenoxyacetic acid that was the main active component of herbicidal formulations, depicted as ARBORICID E50 and ARBORICID EC50.

These production technologies were located in the PCP facility, depicted as Ne 42 (some partial processes, like drying of final product were located also elsewhere). As it was observed gradually at all producers manufacturing 2,4,5-T from sodium 2,4,5-trichlorophenolate (the first was Boehringer/D) the typical skin lesions of workers occured in the second half of the 1960s. It became evident that the compound responsible for these health problems was TCDD formed in the course of condensation of 2,4,5-trichlorophenolate with trichloroacetic acid at higher temperatures in the parasitic side reaction of two molecules of 2,4,5-trichlorophenolate. After information on these problems at other big producers and partial investigations of the health status of workers, the production was immediately stopped, the facility Ne 42 closed and sealed according to a strict decision of the Head of Central Bohemian Regional Hygienic Service in April, 1968. It was very difficult to do anything in assessing the actual toxicological status of the facility as a necessary point of outcome for further decision on decontamination. Permission to entry into the facility was given to the author (then working at the Purkyně Military Medical Institute in Hradec Králové on the problems of TCDD) only because of his underlaying to another hygienic authority under Ministry of Defence.

At the first visit (in 1974) we found (then already) dry residues of production product in the close neighbourhood of technological equipment and generally high level of contamination on all floors. Also service and hygiene rooms (cloakroom, restroom, dushes, WC) were contaminated by dispersed products. Windows were partially broken so that due to communication of technological, service and hygiene rooms, the whole indoor space was contaminated, what was confirmed by on-site toxicological tests in experimental animals.

For the comprehensive assessment of contamination, we have undertaken a strategic procedure, beginning with own synthesis of TCDD, laboratory toxicological and analytical study to assess the level of contamination with TCDD and to find *inter alia* possibility of biological determination of TCDD, taking into account then limited analytical instrumentation for determining trace amounts of TCDD. The toxicological study in mice, guinea pigs and rabbits mainly consisted in toxicometrics and microscopic investigation of internal organs with typical specific histopathological lesions in liver [1] that were suitable for biological detection and identification of TCDD. In spite of extremely low volatility, the TCDD possesses remarkably high inhalation toxicity that was utilised at indoor on-site toxicological assessment using rabbits in cages located on the facility floors. We found the average concentration of 18 ppm of TCDD in all residues of 2,4,5-T butyl ester (using then available GC with electron-capture detector). Based on these observations further proposals for clean-up, decontamination of inner spaces and destruction of the technological equipment in metallurgical processes (together with medical supervision of all hazardous operations by Military Health Services) were tabled that were negotiated on several levels up to General Directory of *CHEMOPETROL*. These works are described in respective research reports, for conclusions and summaries see [2,3].

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Section 3: Pesticide waste management

NATIONAL PLAN OF MANAGEMENT WITH PERSISTENT ORGANIC POLLUTANTS

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1. Abstract

The national implementation plan for the management of plant protection agents, PCBs and polychlorinated terphenyls in Slovenia that contain persistent organic pollutants. The plan is for the management of these substances from 2008 to 2013 and was drafted pursuant to the Stockholm Convention on Persistent Organic Pollutants (Regulation (EC) No. 850/04 of the European Parliament and of the Council). In order to draft this plan, data on the situation regarding the sale and use of plant protection agents had to be collected for individual years. Data was collected on the quantities and types of these substances from merchants and importers. As part of the plan, monitoring of the environmental situation (water, soil, foodstuffs) has begun to take place. An inspection of old stocks of plant protection agents containing POPs was carried out. On the basis of the data collected, a strategy and action plans containing the following were drawn up:

- institutional and legislative measures with the transposition of Community law and a precise definition of the tasks of individual ministries and institutions;
- the frequent regular collection of hazardous waste and old stocks of plant protection agents (from households, agriculture, the environment), and their removal and safe destruction, with the costs for this being borne by the national budget;
- the monitoring of old installations still operating using PCB as dielectric (condensers, transformers), which may be used until 2010;
- identification of areas contaminated with POPs and the preparation of appropriate rehabilitation measures;
- raising of public awareness, provision of information, education and exchange of information;
- monitoring and study of effects of POPs on human health;
- reporting and public information on implementation of the plan.

The paper will present the national plan, the situation in the area of plant protection agents, the progress of specific activities related to implementation of the plan and the results of implementation of individual action plans and priorities in greater detail.

Key words: monitoring, persistent organic pollutant, national plan, water, foodstuff, waste, poisoning

2. Introduction

The preparation of the National Action Plan for the Management of Persistent Organic Pollutants was carried out by the Chemicals Office at the Ministry of Health of the Republic of Slovenia. This project involved the cooperation of the Ministry of the Environment and Spatial Planning, the Ministry of Agriculture, Forestry and Food and many individual experts from other institutions including research institutes, the university, public institutions, NGOs and UNEP (United Nations Environmental Programme). The National Coordination

Committee consisted of 12 people while a total of 57 people, 3 of them from UNEP, worked on the project. The project derives from the Stockholm Convention and was prepared as part of UNEP-GEF project No GF/27322-02-4463.

3. Situation as regards the sale of plant protection products in the Republic of Slovenia between 1997 and 2007

Table and picture 1: Sales of insecticides in the Republic of Slovenia 1997–2007 (in kg of active substance)

1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
85.629	71.084	89.386	97.966	80.905	109.457	118.540	99.888	97.116	109.990	106.463

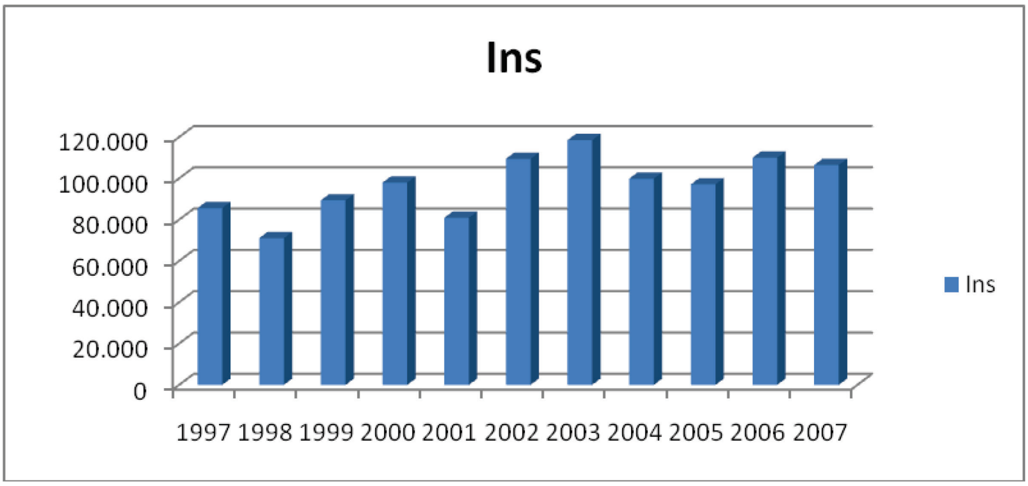


Table and picture 2: Sales of fungicides in the Republic of Slovenia 1997–2007 (in kg of active substance)

1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
892.568	740.611	1.031.901	842.594	932.718	936.687	843.044	1.114.487	967.733	817.281	688.697

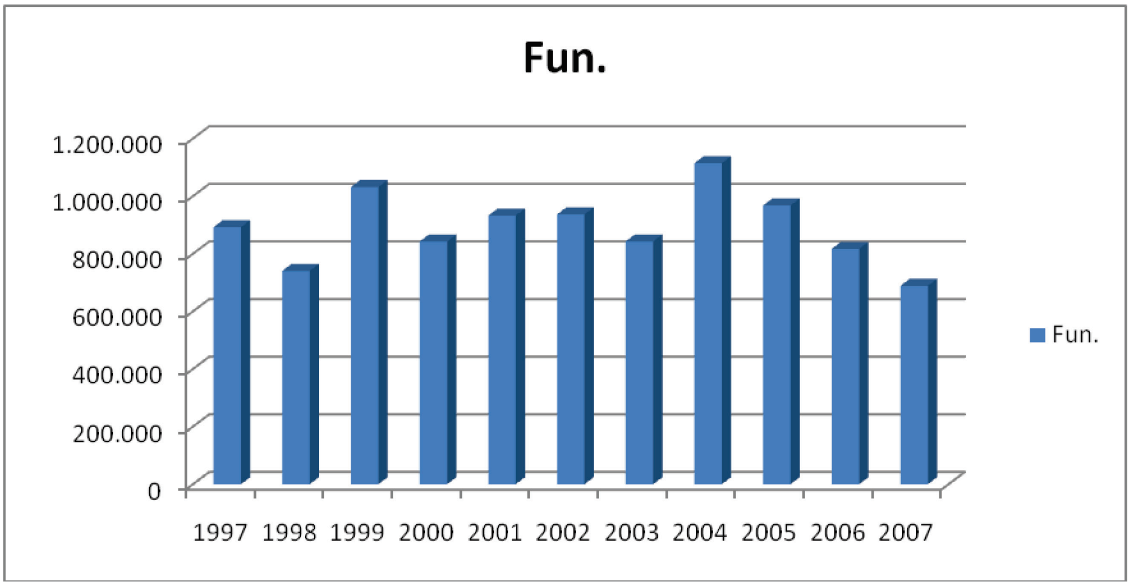


Table and picture 3: Sales of herbicides in the Republic of Slovenia 1997–2007 (in kg of active substance)

1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
263.983	276.553	437.240	408.532	365.894	384.981	332.038	291.164	319.791	321.887	333.995

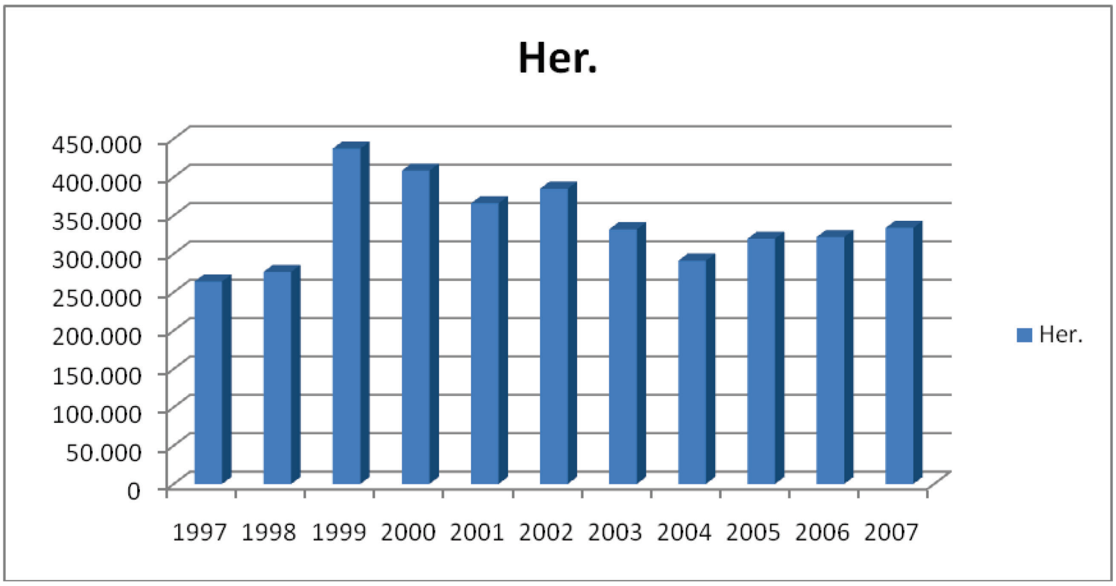
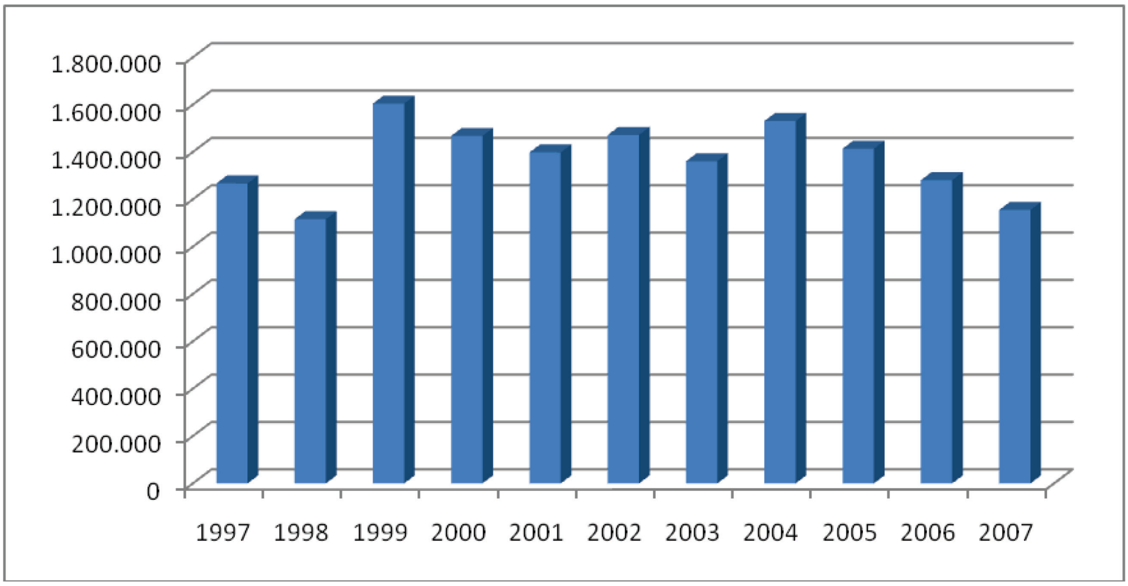
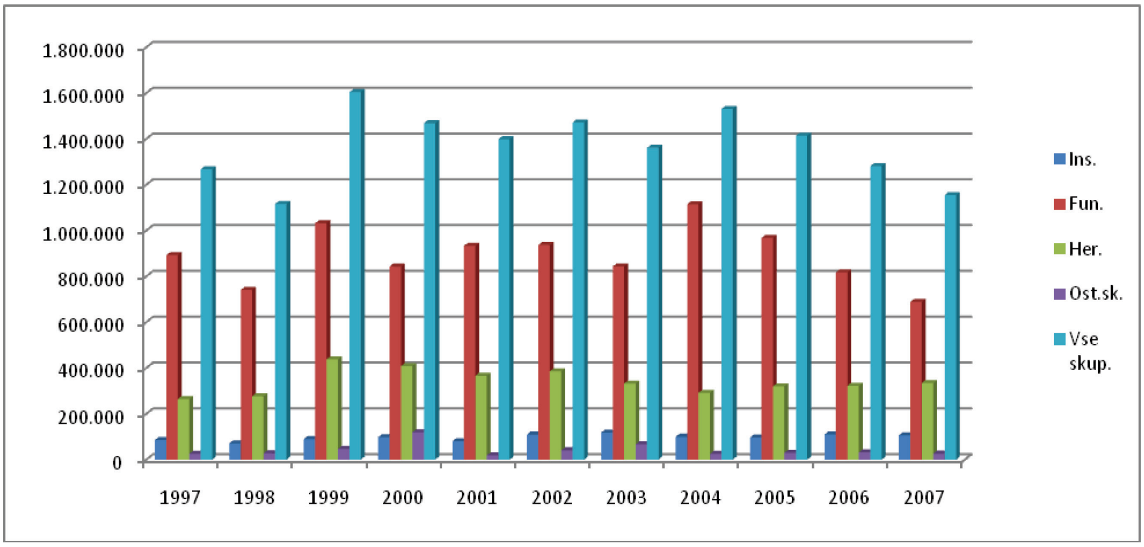


Table and picture 4: Sales of all plant protection products in the Republic of Slovenia 1997–2007 (in kg of active substance)

1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
1.267.143	1.115.851	1.604.519	1.468.110	1.398.268	1.471.927	1.361.051	1.530.735	1.413.967	1.280.980	1.155.221





The Ministry of Agriculture, Forestry and Food of the Republic of Slovenia has been keeping records of sales of plant protection products in the Republic of Slovenia since 1991. Before 1991, the record and verification of sales of these products were managed by the corresponding Yugoslav institution and these figures are unavailable because the data is kept in Belgrade.

4. Operational programmes included in the National Action Plan for the Management of Persistent Organic Pollutants

The individual operational programmes forming part of the National Action Plan for the Management of Persistent Organic Pollutants are:

a/ Operational programme for the disposal of polychlorinated biphenyls and polychlorinated terphenyls for the period 2003 to 2010
The main obligation in this field up to 2010 is to ensure the final processing of all PCB equipment containing oil with a PCB content greater than 500 mg/kg. Equipment containing

oil with a PCB content of between 50 and 500 mg/kg must be decontaminated if such equipment is still operational.

b/ Operational programme to prevent pollution of the aquatic environment with hazardous chlorinated hydrocarbons from diffuse-source pollution
The programme is based on the implementation of already adopted regulations on limit values for emissions from diffuse-source pollution. Monitoring such sources is a constantly ongoing process under the strict supervision of the inspection services of the Ministry of the Environment and Spatial Planning.

c/ Slovenian Agro-Environmental Programme
The objective of this programme is the restructuring of agriculture and a concomitant reduction in the use of plant protection products, particularly because of the increasingly strict control of food production with regard to the presence of these substances.

5. Managing POPs in the Republic of Slovenia

The placing on the market of plant protection products in the Republic of Slovenia is subject to registration and the issuing of a licence. This is regulated by the Plant Protection Products Act. The decision on the registration of a product which enables this product to be used in the Republic of Slovenia is issued by the Phytosanitary Administration of the Republic of Slovenia, a specialist service of the Ministry of Agriculture, Forestry and Food. Consent to this decision must also be given by the Ministry of Health. Trade in plant protection products may be conducted by legal entities or natural persons established in any EU Member State and inscribed in the register for this activity. In order to qualify for inscription in the register they must meet certain prescribed conditions including provisions in connection with premises, equipment, personnel, record-keeping and the submitting of reports. Every legal entity or natural person conducting trade in plant protection products must employ a responsible officer who is responsible for the reception, warehousing, storage and issuing of plant production products. The responsible officer is also responsible for keeping a record of circulation of these products and for supervising and training other employees who work with or come into contact with these products.
Users of plant protection products are subject to the Rules on the responsibilities of users of plant protection products. The Rules prescribe the following:
- the training of responsible officers, vendors and implementers of phytosanitary measures,
- a record of circulation and use of plant protection products, including a record of quantities of plant protection products purchased abroad and in the Republic of Slovenia, quantities of plant protection products (by types and quantities) on the market and quantities of plant protection products stored in companies entered in the register for this activity,
- a prohibition of circulation and use of plant protection products containing POPs,
- supervision of circulation and use of plant protection products,
- control of plant protection product residues,
- review of the situation regarding plant protection products containing POPs in the Republic of Slovenia.

5.1. Use and manufacture of plant protection products containing POPs in the past

After 1945, at which time the Republic of Slovenia was part of the Socialist Federal Republic of Yugoslavia, state regulations were in force which were complemented by legislation at republic level. Between 1945 and 1990 a central record of plant protection product data was kept, which means that the Republic of Slovenia does not have its own data for this period as regards the quantity of plant protection products used in Slovenia in this period. In view of the low intensiveness of farming in Slovenia between 1945 and 1990, the use of plant protection products containing POPs was relatively small. This is also confirmed by the results of analysis of pesticide residues in the soil and in agricultural products. During this period the most common pesticides used in the Republic of Slovenia were DDT (above all to combat the Colorado beetle), endrin (to control voles), toxaphene (to exterminate rats), dieldrin and aldrin. According to data from the Ministry of Agriculture, Forestry and Food, products based on hexachlorobenzene, heptachlor and chlordane were not used between 1957 and 1991.

5.2. Review of old stocks of plant protection products containing POPs

The Republic of Slovenia does not have a record of stocks of the plant protection products that were in use between 1945 and 1990. For this reason the survey on the recording of stocks of plant protection products that also contain POPs was carried out among vendors of these products. There are 239 registered vendors of plant protection products containing POPs in the Republic of Slovenia. They were sent questionnaires prepared by the Chemicals Office, which is a specialist service of the Ministry of Health. Of the questionnaires sent out, 50.8% (121) were returned completed, although just 45.6% (109) were completed correctly.
For the period 1985–2004 the respondents indicated the use or sale of the following plant protection products: aldrin, dieldrin, doripin, lindane, linditin, neocid and endrin. They indicated that for the most part they sold these products up until 1989, when in the majority of cases the use of these substances was prohibited in the Republic of Slovenia.
The survey showed that those vendors who completed the questionnaire do not sell plant protection products containing POPs.
The questionnaire was also sent, with suitably adapted questions, to 68,000 agricultural holdings, in other words to all those who are registered as agricultural producers or whose basic profession is agricultural production. The response to this questionnaire was 26.4% (17,926), and just 3.9% of respondents indicated that they used or stocked plant protection products containing POPs. The results of the survey show that the stocks of plant protection products containing DDT or endrin as an active substance held by these respondents are small. In these 26.4% of answers, or in the 3.9% indicating use/stocks of plant protection products containing POPs, the result is that respondents only hold 10 kg of products in which endrin is an active substance, 1 kg of products based on dieldrin and 75 kg of products based on DDT.

5.3. Programme for monitoring POPs, environmental impacts and health

The review of the monitoring programmes that include POPs covers the following:

- basic elements of the environment: air, soil and water (surface standing and flowing water and underground waters),
- foodstuffs, agricultural produce and materials and products which come into contact with foodstuffs.

Monitoring of the air
Since 1992 Slovenia has been part of the European programme for keeping emissions records (CORINAIR) and the exchange (reporting) of emissions data in the EU. The harmful

substances from the POPs group that are regularly measured in the air are: PCBs, HCHs and HCBs.

Monitoring of underground and surface water and drinking water
The programme of monitoring the quality of surface water includes measurements of aldrin, dieldrin, endrin, DDT isomers (p,p-DDT, o,p-DDT, o,p-DDE, p,p-DDD and o,p-DDD), HCBs and HCH isomers. HCB and HCH content is also determined in sediment to a depth of 15 cm. The number of measuring points and their geographical distribution and the frequency of sampling has changed over the years and is adapted to needs in a specific watercourse area. The compounds listed above are measured or analysed between once and twice a year.

Monitoring of foodstuffs
Examination of foodstuffs on the market and agricultural produce is a constantly ongoing process. Monitoring foodstuffs for POP content covers the following:

- monitoring the presence of pesticides the use of which is prohibited in foodstuffs,
- monitoring the presence of pesticides which are prohibited in foodstuffs but can be the result of an environmental disaster or the consequence of a polluted environment.

Compounds from the POPs group which are included in permanent monitoring of foodstuffs are:

- the group of organophosphorous pesticides (aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene),
- polychlorinated biphenyls (PCB),
- DDT and derivatives, DDD and DDE,
- polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD and PCDF).

Monitoring of wastes
The regulation governing waste management also defines specific types and limit values of individual compounds for every branch of industry. Operational waste monitoring is carried out by companies authorised for waste management.
Compounds from the POPs group which are analysed in hazardous waste are:

- the group of organochlorine pesticides (aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene),
- polychlorinated biphenyls (PCBs),
- DDT and derivatives, DDD and DDE,
- polychlorinated dibenzo-p-dioxins.

6. Pesticide poisoning in the Republic of Slovenia

Between 1997 and 2000 nine fatal cases of poisoning with plant protection products, and a further seventeen hospitalisations, were recorded in Slovenia. The average age of the victims of poisoning was 55. Cases of poisoning were evenly divided between women and men. Of the 9 fatal victims, 5 died as a result of deliberate self-poisoning. This number is growing over time; in 65% of cases poisoning was with insecticides.

7. Conclusion

The above is merely a brief extract of the National Action Plan for the Management of Persistent Organic Pollutants. The plan is already being implemented, although not on the scale envisaged.

The quantities of old plant protection products held by individual vendors and individual agricultural producers is relatively small and does not represent a significant risk for the environment. The state sees to the destruction of these quantities and processing costs are not borne by the owner.|

8. References

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b. Internal acts of Ministry of Agriculture, Forestry and Food of the Republic of Slovenia

OBSOLETE PESTICIDES IN UKRAINE: BACKGROUND, PROGRESS AND CURRENT CHALLENGES

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Abstract. The paper represents the results of an overall analysis and review of the state-of-the-art in the field of obsolete pesticides (OPs) management in Ukraine. Such survey is based mainly on the data provided by the Department of Environmental Safety, Ministry of Environmental Protection, covers the period of time since Ukraine's signature of the Stockholm Convention on POPs in 2001 and observes the subsequent dynamics in solving the OPs problem within the country to present days after Ukraine's becoming a new Party of the Convention in December 2007. It is shown in figures the results of the initial OPs storage sites inventory and recently updated ones, annual amounts of already eliminated OPs and those ones which are planned to be destructed in the nearest time. The paper contains a brief description of the made administrative and technological solutions and the current state in OPs elimination and realization of the activities under the actual contracts with "Elga Co." and "EcoCenter" (Ukraine), "SARPI Dabrowa Gornicza Sp.z.o.o." (Poland) and "AVG Abfallverwertungs-Gesellschaft mbH" (Germany) covered by the State Environmental Fund and local budgets. The gained experience allows to reveal considerable shortcomings of the OPs inventory data and other corresponding gaps which shall be taken into account for finalization of the National Implementation Plan development. Besides, to meet the relevant amendments to the SC adopted at the COP4, it is considered as necessary to represent the available information on the so-called "new" POPs-pesticides in Ukraine, including an overview of their position in the existing regulative frame, within the national OPs inventory and POPs monitoring data.

Key-words: Obsolete pesticides, inventory, elimination, persistent organic pollutants (POPs), Stockholm Convention, National Implementation Plan (NIP)

1. Introduction

Ukraine was one of the most industrialized republics with a highly developed agrarian sector within the former Soviet Union. It became a new independent state in 1991 and now is considered as a country with an economy in transition. In the former USSR, annual production of pesticides reached more than 200 thousand tons, including organochlorine pesticides (OCPs) under the Stockholm Convention on POPs [1,2]. A significant part of them was supplied to Ukraine and used here in different sectors of economy, mainly in agriculture, forestry, military medicine and industry.

As a great amount of obsolete chemicals and other hazardous waste accumulated in the country was recognized as one of priority problems in the country, Ukraine signed the Stockholm Convention on POPs in 2001 and became the Party of this global treaty in December 2007. Besides that, Ukraine is a Party of the Basel Convention on Transboundary Movement of Hazardous Waste since 1999 and the Rotterdam Convention on Prior Informed Consent since 2002. The actual list of the banned pesticides in Ukraine comprises of 87 names of individual and mix preparations, including 10 names of POPs-pesticides.

National environmental policy, including obsolete pesticides and other hazardous chemicals management and elimination, is realized through both special national and regional (local) programs. Besides, certain background national and international activities, which allowed

making the basis for an overall evaluation of the OPs problem in Ukraine, were undertaken during several recent years, and among them it is worth being mentioned the following projects:
«Elimination of Risks Related to Stockpiled Obsolete Pesticides in Ukraine» (1997-2004) and «Assistance to the Ukrainian Environmental Authorities Management of Contaminated Sites» (2003-2005) – the Ministry of Environmental Protection of Ukraine, DEPA-DANCEE and COWI consulting group, Denmark;
«Enabling Activities for the Stockholm Convention on Persistent Organic Pollutants (POPs): National Implementation Plan for Ukraine» (2003-2007) – the Ministry of Environmental Protection of Ukraine, GEF and UNEP;
«Management and Destruction of Obsolete Pesticides in Pilot Oblasts in Ukraine (Cherkasy and L'viv Oblasts)» (2004-2007) – National Agricultural University, National Academy of Sciences and US Environmental Protection Agency;
«Elimination of Acute Risks of Obsolete Pesticides in Ukraine» (since 2008) – NGO "MAMA-86", Milieukontakt International and the Ministry of Foreign Affairs of the Netherlands (Matra Program).

2. Obsolete Pesticides Inventory

At present, the available information on amounts of pesticides which were supplied to Ukraine till 1991 within the Soviet centralized distribution system is rather sophisticated. According to the data provided by the Ministry of Agrarian Policy, the average annual amount of distributed pesticides in Soviet Ukraine run to about 150 thousand tons during 1965-1991, and their annual use in the agrarian sector reached almost 170 thousand tons in 1980s [3]. And now, a huge amount of them is still stored throughout whole Ukraine. The most comprehensive and complex inventory of sites for storage and disposal of the agrochemicals, which are considered as obsolete or banned for use, was initiated by the so-called Order of Three Ministers (2001) and the Decree of the Cabinet of Ministers of Ukraine "On developing the infrastructure for elimination of the banned and obsolete pesticides" (2002). The initial data obtained by regional bodies of the Ministry of Agrarian Policy, the Ministry of Environmental Protection and the Ministry of Health in 2003 were renewed within the NIP development project [3] and the latest search of the information on OPs was recently carried out under the Order of the Ministry of Environmental Protection (2008).
The national inventory of 2003 contained the data on 3 groups of obsolete pesticides: I – banned (58 names in the inventory), II – unusable (162 names), III – unidentified mixtures; the total amount of all revealed (reported) OPs – 19,3 thousand tons - was located in 147 centralized storage facilities and 4983 storehouses of all types of property (agrarian sector only). 33% of the total number of the revealed OPs storage sites do not correspond to the sanitary and hygienic requirements. Unidentified mixtures amounted about 50% of all reported OPs.
Further actualization of the OPs inventory in Ukraine was carried out mainly according to the reports provided by all 27 regional bodies of the Ministry of Environmental Protection. The summarized data for whole Ukraine are shown in Table 1:

Table 1. Total amounts of the obsolete pesticides in Ukraine reported by years, tons.

2003	**2005**	**2006**	**2007**	**2008**
19,341.90	20,998.41	21,048.41	20,257.34	22,097.30

The main problems of OPs calculation remain to be a considerable part of storage sites without any owners, fallibility in estimation of OPs amounts without their direct weighing and a high level of danger to humans during handling with these hazardous chemicals. It is estimated that only 37% of the OPs stocks owners made the required reports according to the national legislation. Besides, the available information is based only on so-called “paper” inventory without any analytical tests or lab identification.
The fact that the represented figures may be considered only as evaluation data is confirmed by the case studies of OPs inventorying carried out on the selected storage sites within the above-mentioned international projects and during the already undertaken elimination activities, i.e. the quantity of unidentified mixtures may run to 75% [4] and the real OPs stockpiles in Ukraine may be even twice higher [5].
At the same time, it is expected that the Order of the Ministry of Environmental Protection No.111 of 04.03.2008 initiated the activities aimed at developing the ministerial OPs inventorying system based on the international methodological approach, including application of such modern tools as informational and PS management systems [6,7].

3. Obsolete Pesticides Elimination

Industrial elimination of OPs in Ukraine started in 2003 at the specialized private enterprise “Elga Co.” in Shostka, Sumy region (oblast), and till now all corresponding activities are financed mainly within the budget program “Waste and Hazardous Chemicals Management” and from regional budgets of local administrations. The “Elga” designed technology for OCPs destruction is based on the process of multiloop low-temperature pyrolysis, the industrial capacity runs to 800 tons per year.

Table 2. Annual and total amounts (gross weight) of the eliminated obsolete pesticides waste in Ukraine, tons brutto.

Elimination tons/year	In Ukraine	Abroad		TOTAL
	Elga	AVG & Dynamyka	Sarpi & NCHWM	
2003-2005	215.5	-	-	215.5
2006	522.2	-	-	522.2
2007	704.7	456.4	-	1,161.1
2008	776.9	432.0	178.3	1,387.2
TOTAL	2,219.3	888.4	178.3	**3,286.0**
	2,219.3	1,066.7		

In the recent two years, it is developed the long-term partnership with EU incinerator plants and now two foreign companies have actual contracts with Ukrainian enterprises – licensed operators in the field of hazardous waste management: “SARPI Dabrowa Gornicza Sp.z.o.o.” (Poland) with “National Center for Hazardous Waste Management” (NCHWM), Kyiv, and “AVG Abfallverwertungs-Gesellschaft mbH” (Germany) with “Dynamyka”, Zaporizhzhya. Ukrainian partners provide OPs collection, packaging and transportation and their foreign partners – hazardous waste destruction. All operations are carried out according to the requirements of the Basel Convention and ADR. The current progress in OPs elimination is shown in figures in Table 2. As for the year 2009, the data are available only for “SARPI Dabrowa Gornicza Sp.z.o.o.” - NCHWM output: 570.8 brutto tons of the eliminated OPs-waste by September.

4. POPs-pesticides in Ukraine

There was only one plant for OCPs production in Ukraine (Kyiv) with the capacity 1000 - 7500 tons of DDT within 1951-1973 [2] or 1954-1975 [3]. Conceivably, DDT production in Kyiv was stopped even later.

The most of initially targeted pesticides under the Stockholm Convention were regulated by the Soviet legislation. The use of DDT, aldrin, endrin, heptachlor, toxaphene and their various preparations was prohibited till 1987. At the COP4, Ukraine seconded the recommendation by the Persistent Organic Pollutants Review Committee to list chlordecone, lindane, alpha- and beta- hexachlorocyclohexane in Annex A of the Convention and endorsed the corresponding amendment to part I of Annex A of the Convention. At present the list of the banned pesticides in Ukraine (1997) includes 8 names of POPs-pesticides and HCH (lindane and hexachlorane (mixture of isomers)) (Table 3). Definitely only mirex and chlordecone were never registered as it is required under the Law of Ukraine "On Pesticides and Agricultural Chemicals", therefore these chemicals could not be imported, produced and used anywhere within the country.

Table 3. Current status of POPs-pesticides in Ukraine.

POPs-pesticides		Use & Production	Inventory, tons	Control & Monitoring
Initially targeted	Aldrin	banned	-	not regular (SES)
	Chlordane	banned	0.2	no data
	Dieldrin	banned		not regular (SES)
	Endrin	banned	1.1	no data
	Heptachlor	banned	13.4	not regular (SES)
	HCB	banned	1.0	not regular in surface water and soils (Hydromet)
	Mirex	not registered	-	-
	Toxaphene	banned	-	no data
	DDT	banned + DDD, DDE	1,744.2	regular in surface water and soils (Hydromet)
"New"	Chlordecone	not registered	-	-
	Lindane (γ-HCH)	banned	273.2	HCH isomers in foodstuff, plants, water, and soils (SES)
	α- and β-HCH	banned as Hexachlorane	516.9 Hexachlorane	

There is no any special environmental POPs monitoring program in Ukraine. The State Hydrometeorological Service (Hydromet) was responsible to carry out regular monitoring studies of two OCPs belonging to the POPs group, such as: DDT (including p,p'-DDE, p,p'-DDT, and p,p'-DDD) and HCB - in surface water, and DDT (including p,p'-DDE, p,p'-DDT, and p,p'-DDD) - in soils, on the territory of whole Ukraine. The summarized corresponding data are available for the period up to 2005 [3]. The State Sanitary and Epidemiological Service of Ukraine (SES) is in charge for the net of laboratories which provide, but not systematically, the data on DDT and its derivatives, HCH isomers, heptachlor, aldrin, dieldrin, HCB and PAHs (benzo(a)pyrene) in foodstuff, plants, water and soils.

A significant part of the POPs monitoring data in different media is available from the research sector, but only some institutes within the National Academy of Sciences carry out long-term studies and the Institute of Occupational Health of the Academy of Medical

Sciences of Ukraine is the leading one for long-term DDT (derivatives), HCH and HCB measurements in humans [3,8].

5. Conclusions

The national and international activities aimed at solving the OPs problem in Ukraine and undertaken during the recent several years demonstrated an undoubted progress in this field. At the same time, the gained experience allowed to reveal considerable shortcomings and indicate new challenges would be met in the nearest future. Most probably, the existing system of OPs inventory in Ukraine is not appropriate to get the real data on the available OPs wastes and requires the prompt measures focused on developing and implementing the corresponding procedures and contemporary managerial tools. In spite of positive advance in OPs elimination and sufficient human resources in Ukraine, it is evident that both the present capacity of the national industry and the state budget will be not enough to solve the whole problem in the foreseeable future. Enhancement of the supervisory system in overall and the measures on decontamination of the sites released from OPs are also strongly needed.

It is expected that the most part of current gaps will be taken into account for formulation of the novel national strategy towards OPs in Ukraine as the basis for finalization of the NIP and its further realization, involving all national stakeholders and including mechanisms of technical assistance both under the Stockholm Convention and within other international or inter-governmental agreements.

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POPs MANAGEMENT IN THE REPUBLIC OF MOLDOVA

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Abstract

The POP problem is considered one of the most stringent environmental problems in the eastern part of Europe, because of the lack of adequate infrastructure to collect and store agriculture chemicals and of a proper management of household and hazardous wastes.

Current environmental problems in Moldova are largely the result of past ineffective and inefficient management as well as declining environmental expenditures and investment. The POP problems in Moldova are mostly related to obsolete pesticides from the agricultural sector and PCBs in the energy sector.

In November 2003, the Moldovan authorities have started the repackaging and transportation of obsolete pesticide stockpiles scattered across the country into a limited number of warehouses. Approximately 3,300 tons of chemical wastes have been collected in 35 central storehouses for further treatment.

Recognizing that the long term storage of obsolete pesticides is not a sustainable option since a series of deficiencies revealed in the process of repackaging and storage raised concerns about the integrity and security of the storage facilities, the Ministry of Ecology and Natural Resources submited in 2005 a project proposal on Persistent Organic Pollutants Stockpiles Management and Destruction to the GEF seeking assistance for final disposal of the POPs obsolete pesticides and PCBs, as well as for strengthening POPs national management capacities.

In 2007-2008, more then 2200 tons of obsolete pesticides and PCB containing electrical capacitors were shipped in France and incinerated. The remaining part of about 2000 tons obsolete pesticides from central stories will be disposed of with the assistance from NATO and Moldovan Government in the near future.

There are several other activities undertaken by Moldovan Government in order to improve the POPs Management in the country such as *modification of the regulatory framework for POPs management* which is currently implemented; *upgrading and strengthening of existing laboratories for POPs analysis, national inventory of POP residuals and mapping of polluted areas, awareness and educational activities,* other activities which will contribute to a sustainable POPs management in Moldova.

Key-words: Persistent Organic Pollutants (POPs), the Stockholm Convention on POPs, sustainable POPs management, obsolete pesticides (OP), polychlorinated biphenyls (PCBs).

Introduction

The Republic of Moldova lies in the south-east part of Europe and gained its independence in 1991, after the collapse of the Soviet Union. The country has a population of 4.3 million – 45% urban and 54% rural. Its economy is primarily agricultural with intense use of its natural resources and biodiversity.

During the Soviet era, about 1000 pesticide stores pesticide were built on collective farms. During 1991-2003, most of them were destroyed or dismantled. Of those that remained, only 20% were maintained in satisfactory condition. The lack of strategy for pesticide management resulted in pesticides being kept in many different depots across the country, some of which were close to residential areas. They were often sub-standard and not maintained. Improper storage condition, including storage in the open, led to the deterioration of the packaging, release of the pesticide in the environment and contamination of area around the stores.

Old and banned pesticides are one of the most severe environmental problems in Moldova, because of the lack of adequate infrastructure to collect and store chemicals and a lack of proper management of household and hazardous wastes. Also of concern are polychlorinated biphenyls (PCBs), which were used in dielectric oil for the electrical equipment.

The Problem – Contaminated sites and stockpiles

In the past, large quantities of pesticides were used – between 1950-1990s an estimated 560,000 tons of pesticides were used including large quantities of persistent organochlorine compounds. The absence of controls over pesticides has resulted in the accumulation of more than 7,300 tons, including about 4,000 tons buried at a pesticide dump in Cismichioi, in the South of Moldova. Approximately 3,300 tons were stored in 33 central storehouses, where obsolete pesticides and other chemicals from decentralized warehouses have been collected for further treatment.

Local authorities and the population are not aware of the potential dangers around pesticide stores. Old stores are used as a source of free construction materials for household needs. Adjacent areas are also used for grazing or agriculture, which results in people and farm animals being exposed to pesticides through contact with contaminated soil. The Moldovan environmental authorities realized that the long term storage of obsolete pesticides was not a sustainable option since it is difficult to ensure the proper storage of pesticides, even after these have been repackaged.

PCBs have never been produced in the Republic of Moldova, all of them being imported. Their utilization in some sectors has been discontinued or prohibited in the 1980s. However, PCBs continue to be used in power installations and other types of equipment. A preliminary inventory made in Moldova in 2003 estimated the total amount of dielectric oil from electric installations, which must be considered potentially contaminated with PCBs, at approximately 30,000 tons, including 23,300 tons in high voltage transformers, 5,400 tons in circuit breakers and 400 tons in capacitors.

Developing a National Implementation Plan

During the last decade POPs have been recognized as a national priority problem and Moldova became a Party to the Stockholm Convention on Persistent Organic Pollutants. With support of the Global Environment Facility (GEF) Moldova developed its National Implementation Plan (NIP) for the Stockholm Convention[1].

An initial step was to compile a preliminary inventory of stockpiles of POP pesticides and PCBs. An environmental impact assessment done as a follow-up estimated that there were about one thousand sites (demolished, abandoned or empty pesticides storehouses, pesticide mixing facilities, and adjacent zones) with an average area of less or about of 1 ha, which were likely contaminated and would require a detailed inventory, risk assessment, development of remediation measures and their implementation. A more recent investigation by the State Ecological Inspectorate estimated the total area of pesticides contaminated lands in the country to be between 800-1000 hectares.

According to provisions of the National Implementation Plan and Moldovan Government Decision no. 81 dated February 2009 on PCB Regulation[2] all power equipment in the country (e.g. transformers, switches, breakers, inductors and other receptacles containing liquid stocks) will have to be checked for PCB content, to be labeled accordingly and – depending on the results – dealt with in view of PCB removal. In this regard a comprehensive national PCB inventory was launched in September 2008 under the GEF/WB "POPs Stockpiles Management and Destruction Project".

[1] http://www.moldovapops.md/app/includes/files/nip_eng.pdf
[2] http://www.moldovapops.md/app/includes/files/PCB%20Regulation%20Eng.pdf

What was done?

An early initiative, which started in November 2003, was to repackage and consolidate obsolete pesticide stocks scattered across the country into a limited number of stores. Then, the Ministry of Ecology and Natural Resources (MENR) developed a proposal for the *Persistent Organic Pollutants Stockpiles Management and Destruction Project* and sought financial assistance from the GEF to strengthen national POPs management capacities and to dispose obsolete POP pesticides and PCBs. The Ministry started the project in March 2006.

The Moldovan Government also applied for and received technical assistance support from Canada POPs Trust Fund to identify and implement cost-efficient best available techniques (BATs) for remediation of areas polluted with POP pesticides and clean-up of PCB-contaminated oil from power equipment. The government engaged an international company to identify and test cost-efficient best available techniques to remediate areas polluted with POP pesticides. The testing of two alternatives techniques for decontamination of POP polluted areas in three pilot sites started in March 2009.

Outcomes/impacts of the project

Under daily supervision of Danish and local consultants, between March 2007 and July 2008, 1292 tons of obsolete pesticides in 13 stores, which were selected based on their risk assessment, have been repacked in UN containers and incinerated in a French licensed facility in accordance with best environmental practices. Over this period, the same French company also disposed of 934 tons of obsolete PCB containing capacitors. The remaining part of obsolete pesticide stockpiles from 22 central stores (about 2000 tons) will be disposed of with assistance from NATO.

More than 100 local officials (plant protection, environmental inspectors and representatives of local authorities) were trained on how to handle the obsolete chemicals in order to prevent the contamination of environment. While the main aim was to improve environmental conditions in the country, additional benefits include:

- *Building national capacity for the handling and management of hazardous waste including legal and institutional arrangements, raising laboratory analysis and information management capacity, and obtaining knowledge and know-how;*
- *Poverty reduction and economic growth, especially in rural areas, through creation of opportunities for producing clean/organic agricultural products.*

Costs

Moldova received in total USD 6.35 million from GEF for the stockpiles management and destruction project, which was supplemented by USD 1.6 million from the government and 2.3 million as in-kind contributions and other sources of funding. The total cost of destruction activities within the project was about 3 million Euros from which 876,000 Euros came from the Moldovan Government (State Budget and the National Ecological Fund). At the same time Moldova received CAD 444,000 from the Canada POPs Fund for the demonstration projects.

Lessons learned

The outcomes of the project were considered successful due to the fact that environmental issues caused by POPs and especially those identified as national priorities to protect human health and the environment such as organochlorined pesticides in agriculture sector and PCBs in the energy sector have been addressed.

The second main factor of success was the involvement of local stakeholders. During the development of the NIP and Environmental and Social Assessment of the project proposal, a wide group of local stakeholders, including government, NGOs and local communities affected by POPs pollution, have been involved. The consensus reached during this consultation process has resulted in an agreed National Action Plan, to which all projects contribute in a substantial way.

Next steps

The Moldovan Government will continue to work on meeting all requirements under the Stockholm Convention and other international agreement on POPs and to mobilise international assistance for projects. It is also expected that local officials that were trained in the sound management of POPs will be able to disseminate this knowledge to others as efforts are made to clean up and decontaminate the remaining sites in Moldova. If the site clean-up pilots are successful, the approaches will be used to clean up the other contaminated sites in the country.

The government has already received funding to implement other projects such as *modification of the regulatory framework for POPs management* and *upgrading and strengthening of existing laboratories for POPs analysis*. Moldova will also update its National Implementation Plan to include activities which were not foreseen in 2003 when the plan was first done. Addressing the release of unintentional POPs and the strengthening of monitoring and laboratory capacities are two areas that need further effort.

OLD ECOLOGICAL BURDEN IN MACEDONIA. WASTE HCH-ISOMERS DISPOSAL

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Abstract
HCH-isomers derivatives are known to be of high risk to the human health and the environment. They are highly toxic, persistent, bio-accumulative and long range trans-boundary pollutants.
Generated as a waste from the lindane production, the HCH-isomers were disposed in the period of rapid industrialization (1964-77) by the Organic Chemical Plant OHIS creating several heavily contaminated sites in an area of some 5000 sqm located in vicinity of the capital Skopje, very near the main river Vardar. The active component, gamma-hexachlorocyclohexane, was produced by photo-chlorination of benzene. The produced mixture contains also other HCH-isomers, i.e. alfa, beta and delta. Being poor insecticides, these ballast isomers were treated as a waste and some 25-30,000 tonnes were 'temporary' discharged in a dumpsite. In that purpose a concrete pool was constructed, filled with the ballast HCH-isomers and covered with a layer of soil. Pool's top was not properly protected against penetration of rainfalls, and the bottom was not properly protected against leakage.
Several detailed studies as well as the investigation of the level of contamination of the dumpsite(s) were conducted in order to provide proper conditions for clean-up of the contaminated sites and the elimination of the HCH-isomers from the country. The general parameters are identified and the picture will be completed with the final data to provide pre-conditions for final action for performance of environmentally sound HCH waste disposal and area remediation.
With the international support a serious environmental problem will be closed. The main beneficiaries will be the population of Macedonia and the region as a whole.

Key- words
HCH-isomers, disposal, landfill, health, environment, remediation, costs

Introduction
Hexachlorocyclohexane (HCH) is a synthetic chemical that exists in eight chemical forms called isomers. The different isomers are named according to the position of the hydrogen atoms in the structure of the chemical. One of these forms, gamma-HCH (or γ-HCH, commonly called lindane), is produced and used as an insecticide on fruit, vegetables, and forest crops, and animals and animal premises. It is a white solid with vapour pressure at 20^{o}C (9,4 x 10^{-6} mmHg) high enough to be detected in the air. The vapor is colorless and has a slight musty odor when it is present at 12 or more parts HCH per million parts air (ppm).
Lindane and the other HCH isomers are mobile in the environment, and through long-range atmospheric transport, are deposited in the Arctic, where they have been detected in air, surface water, groundwater, sediment, soil, ice, snow pack, fish, wildlife, and humans.

You will be directly exposed to γ-HCH if you use a prescription medication that contains this compound in order to treat and/or control scabies and head lice. You can also be exposed to small amounts of γ-HCH and the other isomers (α-, β-, and δ-HCH) by eating foods that may

be contaminated with these compounds. Exposure to the HCH isomers is also possible from ingesting contaminated drinking water, breathing contaminated air, or having contact with soil or water at hazardous waste sites that may contain these compounds.
Other HCH-isomers can as well enter the human body when eating food or drink water contaminated with HCH. Inhaling γ-HCH or other isomers of HCH in air can also lead to entry of these chemicals into the lungs. γ-HCH can be absorbed through the skin when it is used as a lotion, cream, or shampoo for the treatment and/or control of scabies and body lice. In general, HCH isomers and the products formed from them, once in the body, can be temporarily stored in body fat. Among the HCH isomers, β-HCH leaves the body the most slowly. α-HCH, δ-HCH, and γ-HCH, and the products formed from them in the body, are more rapidly excreted in the urine; small amounts leave in the feces and exhaled air. HCH breaks down in the body to many other substances; these include various chlorophenols, some of which have toxic properties.
In humans, breathing toxic amounts of γ-HCH and/or α-, β-, and δ-HCH can result in blood disorders, dizziness, headaches, and possible changes in the levels of sex hormones in the blood.
Among other HCH-isomers, Lindane is more toxic to insects than DDT and it bioaccumulates rapidly in organisms. It has a half-life of 2.3 to 13 days in air, 30 to 300 days in water, 50 days in sediments and two years in soil. It is stable to light, high temperatures and acid but it can be hydrolyzed at high pH. Lindane degrades very slowly by microbial action. Lindane is more water-soluble and volatile than other chlorinated organic chemicals.
Considering the health impact, lindane is considered to be a carcinogen and has been associated with liver cancer. Medical studies also have shown that there is evidence of antiandriogenic 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. Nevertheless, the elimination of lindane from the body is fairly rapid once its use has been discontinued.

Background Information

Lindane production plant
The industrial chemical plant OHIS AD is located at the south-eastern edge of the city of Skopje near the Vardar River. The Lindane complex in OHIS AD – Skopje had the plants HCH, Lindane and TCB, where HCH, Lindane, three-chlorobenzene and hydrochloric acid were produced, respectively. The Lindane complex was gradually put into function since 1964 and was functioning until 1977, when it was abandoned and stopped for ecological reasons and change of the market conditions.
In the HCH Plant technical hexa-chlorine-cyclo-hexane with gamma isomer of 12-14% was produced with photosynthesis of chlorine and benzene. This technical HCH was further treated to obtain pure gamma isomer 99,9%, i. e. Lindane, while the non-active isomers such as alpha, beta and delta which were extracted in the Lindane Plant were a material for obtaining three-chlorobenzene and hydrochloric acid in the TCB Plant. Gamma isomer was extracted from technical HCH with methanol in a closed-loop process. The process of obtaining three-chlorobenzene and hydrochloric acid from the non-active isomers was performed with thermal degradation in presence of active coal as a catalyst.

HCH dumps

After gamma isomer was extracted from the technical HCH, the rest of inactive isomers (alpha, beta and delta-isomers) were dumped on the very site. The efforts to utilize them for the production of TCB (trichlorobenzene) and HCl failed. Alpha and beta isomers are dumped on one dump and gamma isomer on 5 smaller dumps. Landfills were constructed with supporting concrete walls, bottom lining, and covered with soil. The bigger one has no bottom lining.

Bigger dump (100 m x 50 m x 5 m) and smaller one (35 m x 35 x 0,5 m and 4 m high) contain some 25,000-30,000 t (25,000 m^3) of alpha and beta and delta isomers and soil.

The average composition of isomers mixture is:

- Alpha isomer 84,75%
- Gamma + betta 0,55%
- Beta isomer 12,27%
- Contents of water 0,5%
- Methanol 0,5%

Composition of the isomers of HCH in delta paste:

- Alpha 22-26%
- Beta 5- 7%
- Gamma 16-19%
- Delta 38-50%

Environmental and health impacts

Environmental Impact of HCH Isomers

- Impact of HCH isomers on soil

The impact of former production and existing HCH dump site on soil could be from the environmental view of point rated as **tolerant**, or (related to the long period of the abandoning of the production) as **low** (EPTISA study, 2007).

- Impact on groundwater

Results from EPTISA study (2007) showed the existence of HCH isomers and other organic pollutants in ground water. Some of reported values do exceed legal allowances according to Dutch standards. Due to the biodegradation potential of HCH, and low solubility in water, the impact of former production and likely from existing HCH dump site on ground water could be rated from the environmental point of view as **moderate**.

- Surface Water Impacts

Based on the data from the period when OHIS plant was still in operation, and surface water pollution by waste water was serious, it could be assumed that the impact on surface water from the existing landfills, after the production was phased out, does not exist any more (EPTISA study, 2007).

- Impact on air

The residence time (half life time) of Lindane and isomers in air (water and soil) depends of the hydro-meteorological conditions and it ranges in months. From this point of view, impact of HCH dump site on the environment is rated as **negligible** (EPTISA study, 2007).

Health Impacts

Generally there are hazard identification and potential health risk due to stored HCH isomers in enormous quantities for employees and population in Skopje.

Table 1. Distribution of hazards, possible health effects and potential number of excised people by hazardous sides

Hazardous site	Hazards	Possible health effects	Potential number of excised people
OHIS Skopje	Organic chemical plant; HCH isomers are stored; waste water into Vardar River,	Carcinogenic on humans (liver, kidney and immune system diseases	470.000 inhabitants 700 workers

Conclusions – recommended scenarios
Three former studies on HCH-dump sites in OHIS did produce similar scenarios, equally useful and applicable.

UNEP Study (2001) alternatives	
Alternative 1: Demolition, excavation and off-site disposal of debris and soil	**Alternative 2: Demolition /excavation/ soil incineration and debris disposal**
Conducting investigations of soil and groundwater and determining contamination characteristics of floors, walls, equipment and roofs for decommissioning purposes. Preparing a remediation plan, including a detailed work plan and a safety plan. Removing all obsolete equipment. Demolishing the building structures. Excavating the contaminated soil in the area of the plant. Transporting building debris and soil (possibly also obsolete equipment) to a secure landfill site. Backfilling the excavation pit with clean soil. Reusing the area, for example, for industrial development.	Conducting investigations in soil and ground water and determining the contamination characteristics of floors, walls, equipment and roofs for decommissioning purposes. Preparing a remediation plan, including a detailed work plan and a safety plan. Removing all obsolete equipment Demolishing the building structures. Excavating the contaminated soil in the area of the plant. Transporting building debris (possibly also obsolete equipment) to a secure landfill site. Transporting excavated soil to the incineration plant. Incinerating the soil. Backfilling the excavation pit with clean soil or treated soil from the incineration process. Reusing the area, for example, for industrial development.
Estimated costs in USD: 255.000*	**Estimated costs in USD: 365,400****

* Excludes 5,830,000 USD for secure landfill planning, design and management
**Excludes the design and construction costs for the incineration system

ENACON Study (2008) alternatives			
Alternative 1: Capping of both HCH dumps	**Alternative 2: Excavation of dumped HCH waste and HCH-contaminated soil with off-site disposal**	**Alternative 3: Excavation of dumped HCH waste and HCH-contaminated soil with on-site waste treatment using Gas Phase Chemical Reduction and treatment of soil by biodegradation**	**Alternative 4: Excavation of dumped HCH waste and HCH-contaminated soil with on-site waste treatment using Base Catalyzed Decomposition and treatment of soil by biodegradation**

Site preparation (removal of bush, disassembly of iron construction on the top of dump of α- and β- HCH); Installation of the impermeable base Construction of a grading fill on both dumps; Capping of the dumps, re-vegetation; Monitoring.	Site preparation (removal of bush, disassembly of iron construction on the top of dump of α- and β- HCH); Construction of off-site permanently controlled hazardous waste landfill; Excavation of dumped waste, contaminated soil overlying and underlying both dumps as well as contaminated soil surrounding the δ- HCH dump and concrete constructions in both dumps; Transportation of excavated waste, contaminated soil and construction debris to the newly installed hazardous waste landfill; Monitoring.	Site preparation (removal of bush, disassembly of iron construction on the top of dump of α- and β- HCH), Selective excavation of dumped waste, contaminated soil overlying and underlying layers in both dumps as well as contaminated soil surrounding the δ- HCH dump and concrete constructions in both dumps. Treatment of excavated HCH waste on-site using Gas Phase Chemical Reduction technique. Treatment of excavated HCH-contaminated soil and debris (after crashing) using on-site biodegradation. Backfilling of excavated pit by treated soil and land filling of treated debris as non-hazardous waste. Monitoring.	Site preparation (removal of bush, disassembly of iron construction on the top of dump of α- and β- HCH), Selective excavation of dumped waste, contaminated soil overlying and underlying layers in both dumps as well as contaminated soil surrounding the δ- HCH dump and concrete constructions in both dumps. Treatment of excavated HCH waste on-site using Base Catalyzed Destruction (BCD) technique. Treatment of excavated HCH-contaminated soil and debris (after crashing) using on-site biodegradation (DARAMEND). Backfilling of excavated pit by treated soil and land filling of treated debris as non-hazardous waste Monitoring.
Estimated Cost (Million Euro)			
0.5 – 1.2	**2.8**	**16.8**	**36.1**

EPTISA Study (2007) alternatives							
In situ			**On site**	**Ex situ**			
Phytoremediation	**Thermal treatment**	**Chemical Reduction**	**Capping – mitigation measure**	**Excavation and Based Catalyzed Decomposition**	**Excavation and thermal treatment – Extern**	**Excavation and thermal treatment – Cement Kiln**	**Excavation and off site disposal**
Total Costs (Euro)							
/	/	/	**109.807**	**4.575.003**	**8.932.366**	**2.536.038**	**1.230.124**

Phytoremediation with a bacterium *Pseudomonas aeruginosa* ITRC-5 that mediates the degradation of all four isomers of HCH under aerobic conditions, both in liquid-culture and contaminated soils. After phytoremediation can the soil be disposed on Drisla landfill for intermediate cover purposes.

Thermal treatment whereby conventional 3-phase electricity is split into 6 separate electrical phases, thus providing improved subsurface heat distribution. Six electrodes are placed in a hexagonal pattern around the area to be treated. Each one of the 6 phases is delivered to a single electrode. The temperature of the soil increases due to the passing of the AC current through the soil moisture. At higher temperatures the vapour pressure of present organics is higher, they readily volatise and their removal is easier. Heating the soil also dries out the soil moisture and creates steam, which increases the permeability of the formation (which can be helpful in low permeability materials) and strips higher boiling contaminants that may not be removed alone.

Chemical Reduction in combination with biopiling, while reducing material such as Daramend will be used to reduce HCH isomers on site. The treatment will be for a minimum period of 1 year and will also consume big areas to set up piles for the aerating treatment. A dilution of the concentration from 500 g to 100 mg would have to be initiated which would require a dilution factor of 1:5000. The material would be able to be used afterwards as topsoil material at Drisla landfill.

Capping – mitigation measure - main measure is to cover the dumpsite with hermetic cover to minimize the intrusion of atmospheric rainfalls and leaching of soluble part of the waste. Also the air emission will be minimized. For this purpose the artificial material (PHD plastic) or soil could be used.

Excavation and Base Catalyzed Decomposition involves treatment of liquid and solid wastes in the presence of a reagent mixture consisting of a high boiling point hydrocarbon such as fuel oil, sodium hydroxide and a proprietary catalyst.

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ENVIRONMENTALLY SOUND DISPOSAL OF DDT – AN EXAMPLE FROM TANZANIA

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1 Abstract

In 2003, the National Environmental Management Council (NEMC) of Tanzania carried out a countrywide survey to identify stockpiles of obsolete pesticides and POPs chemicals. Approx. 50 tons of obsolete DDT were identified in a storehouse near the Pangani River and the Old Korogwe residential area. These stocks were found under poor storage conditions. The site was given a very high priority for disposal based on the significant quantity and the risks for public health and the environment. As the store was considered to be one of the most dangerous hotspots in the world, the Government of Tanzania asked Germany for help to eliminate this hazardous burden. In January 2008, German Technical Cooperation (GTZ) carried out a disposal operation including comprehensive safeguarding on site. A total of 86 tons of DDT and 20 tons of DDT-contaminated construction material from the dismantled store were removed and shipped to Germany for final disposal in a hazardous waste incinerator at the end of October 2008. The disposal operation was a joint GTZ and NEMC activity and was conducted in cooperation with the African Stockpile Programme (ASP). The presentation describes all steps of the disposal operation, the necessary safety precautions and the serious problems with the international transport.

Key words

DDT, Tanzania, waste disposal, incineration, hazardous waste incinerator, POPs chemicals

2 Background

Under the African Stockpile Programme (ASP) of the World Bank and FAO, a nationwide inventory of obsolete pesticides was carried out in Tanzania between 1997 and 2000. In the course of this operation, over 50 tons of DDT and reportedly an unknown quantity of the insecticide *Thiodan* were found in Korogwe, a small town about 180 km north of the capital Dar Es Salaam. The unsecured and totally unsuitable store with this large quantity of DDT granulate was described by both Greenpeace and the International POPs Elimination Project (IPEN) as one of the most dangerous hotspots of POPs chemicals in the world.

2.1 Old Korogwe pesticide store

According to information from the Ministry of Agriculture, Food and Cooperatives (Kilimo), the pesticides had been stored on the site of a former sisal factory on the outskirts of Old Korogwe since the start of the 1980s. As a result of incorrect storage, a hazardous mix developed of degraded plastic, paper bags and loose DDT piled up there. Despite a temporary measure to secure the site carried out by the National Environment Management Council of Tanzania (NEMC) under the ASP project, the pesticides remained exposed to wind and weather, and were accordingly able to escape into the environment. The DDT was also the source of constant odour nuisance, which significantly impacted the quality of life (and health) of the people living in the neighbourhood of the store.

It was not possible to determine the manufacturer of the DDT, only the company which had produced the 5% granulate. This was a local company, SAPA Chemical Limited, from Dar Es Salaam. However, the chemical analyses failed to identify any of the Thiodan shown in the inventory.

The pesticide store in Old Korogwe – before disposal

2.2 Risk assessment

Under the Stockholm Convention, DDT is one of the POPs chemicals identified as highly toxic and persistent, use of which has since been discouraged worldwide under the Convention.
The store was within 50 m of the banks of the Pangani River, the only source of drinking water for the people in Old Korogwe. The washing area, used daily by the inhabitants, is also in the direct vicinity of the store. Small farmers' goats and cows also graze constantly on the extensive site of the former sisal factory. Just a few metres from the store is an office of the *Micro Credit Bank for Women of Tanzania*, regularly frequented by numbers of women with children. The children play around the DDT store, and are accordingly constantly exposed to the DDT odour.
Over the years, there have been frequent reports in press and TV on the hazards and risks to people and the environment from the store in Old Korogwe. The people living in the neighbourhood of the store complained increasingly in the media of diseases which they blamed on the DDT. Local NGOs, including AGNEDA and IPEN, took up the cause, and finally the problem was debated in the Tanzanian Parliament. The Government promised relief to those affected.

2.3 Conclusions and project formulation

Given the acute hazard to people and environment in Old Korogwe, immediate action on the store was required, regardless of who was responsible for procurement of the DDT. In August 2004, the Tanzanian Government applied officially for German Government assistance in eliminating the Old Korogwe DDT store. In November 2006 the German Federal Ministry for Economic Cooperation and Development (BMZ) commissioned GTZ to dispose of the DDT from Korogwe. The GTZ Convention Project Chemical Safety was given responsibility for project management.

3 Preparation for the measure

Representing the Governments of Tanzania and Germany, the NEMC and GTZ entered into an agreement on the disposal of the DDT store. This included a provision that GTZ would train local experts, thus enabling the NEMC to carry out further disposal measures in Tanzania itself.
A German commercial disposal company, Currenta GmbH, Leverkusen, was commissioned with the practical work on securing and disposing of the DDT. The order went beyond the decontamination of the store to cover demolition of the complete store and transport of all the construction waste to Germany for safe disposal in a special hazardous waste incineration

(HWI) plant. The entire measure was managed, coordinated and monitored by the GTZ chemical project.

3.1 Public briefing, training local experts

The project team arrived in Old Korogwe on 14 January 2008 and started with preparations on site. These included the project management introducing themselves to the local district authorities and the chiefs in Old Korogwe. The first activity agreed was a public briefing at the store itself.
One purpose of the public briefing was to inform the chiefs of the population and directly affected neighbours of the store in Old Korogwe about the start and nature of the activities. The goal was to avoid concern among people around the camp, as DDT had become an extremely sensitive issue in Old Korogwe.

3.2 Implementing safety and disposal measures in Old Korogwe

3.2.1 Operational stages: Currenta as the disposal company was responsible for securing DDT on site, demolishing the store, transporting the DDT to Germany and environmentally safe disposal of the DDT in a special HWI. The project included the following activities:

- Submitting an Environmental Management Plan as a guideline for the approach, work safety, environmental protection and transport of the DDT.
- Obtaining the necessary documentation under the Basle Convention requirements, such as import permits for the waste in Germany, and the necessary transboundary shipment documents for international sea transport of the DDT from Tanzania to Germany.
- Procuring the necessary working, safety and packaging materials for the field operation in Tanzania.
- Packing the DDT and other contaminated associated waste in UN-approved containers in accordance with the international regulations for the international transport of hazardous waste (IMDG Code).
- Cleaning and decontaminating the DDT store in Old Korogwe.
- Demolishing the pesticide store and packing the construction material in UN-approved packaging materials in accordance with the IMDG Code.
- Transport of the hazardous waste (DDT, associated waste and construction material) from Korogwe to the HWI in Germany.
- Environmentally safe disposal of the waste in a suitable (state of the art) HWI in accordance with OECD standards in Dormagen, Germany.

Currenta was also responsible for

- the entire logistics in Germany and Tanzania
- local security during the entire safety measure (collection and repackaging of all obsolete pesticides in an environmentally sound manner)
- training local NEMC personnel (8 labourers, 2 NEMC staff)
- documenting the various stages in the whole disposal process.

3.2.2 Fieldwork: Work in Old Korogwe started with setting up the 10 transport containers supplied. The containers were unloaded with great effort using a special crane.

Work on the store itself began with

- Securing the store. The entire warehouse was wrapped in PE film, and an airlock was fitted up. The aim was to ensure that no DDT dust could escape to the environment during the work on the store.
- Setting up a **black zone**, an **intermediate zone** and a **white zone**.
- The black zone is the working area in the store. The intermediate zone separates the white zone from the black zone through an airlock and a boot washer. All material has to be transported into the store through the airlock. In the white zone, the only work permitted is storing DDT after packaging.
- In the black zone the DDT granular is filled into black PE bags. The bags are then taken to the airlock, where they are packed again into another (transparent) PE bag. The DDT is then taken through the airlock to the intermediate zone, where the bags are finally packed into Big Bags and transferred to the white zone for storage.

Filling DDTs into black PE bags

Packing PE bags with DDTs into big-bags

- The Big Bags and transport containers were labelled in accordance with the IMDG Code for maritime transport of dangerous goods.

Big-bags are ready to be transported

- After packing all the DDT in Big Bags, the entire interior and external walls of the store was decontaminated three times using caustic soda.
- The store was subsequently demolished down to the foundations.
- The construction waste (except for the metal roofing plates) was also packed in Big Bags.
- The nine transport containers with the refuse (106 tons of DDT and contaminated construction waste) and one container with the equipment were loaded onto trucks with a special crane, and subsequently transported in convoy to Dar Es Salaam. After customs clearance at the port, all the containers were loaded onto the vessel *MS Stefania* for transport to Germany.
- Because of the heavy dust formation in the store, all the workers had to wear full protective clothing (chemical protective clothing with full face mask and special filter, disposable overall, safety boots, protective gloves).

- To prevent contamination, all workers had to decontaminate their boots with caustic soda in the boot washer on leaving the store, and remove their overalls.

Before the start of work, all local workers were examined by a doctor for fitness. Because of the extreme climatic conditions, two shifts were employed, changing over every half hour. All activities were completed on **30 January 2008** and the cleared and decontaminated site of the former DDT store was handed over to the Director of the NEMC.

3.2.3 Transport: Instead of shipping the containers to Germany via Saudi Arabia and through the Suez Canal, it was necessary to take the ten containers via Durban (South Africa) to Hamburg and then transport them by truck to the Dormagen HWI. The harbourmaster at Jeddah (Saudi Arabia) refused permission to trans-load the containers with the waste onto another ship. The reason for this is the apparent difference in international definition of the Basle Convention – the difference between **transit of waste** (the waste stays on the same ship) and **transfer of waste** (the ships are changed, and the waste is offloaded at the harbour, involving a brief period on shore). Finally, on 9 September 2008 the ten containers arrived at Currenta's HWI in Dormagen, Germany.

4 Disposal of the DDT at SMV Dormagen

At the Dormagen HWI, a total of **85.606 tons of DDT granulate and 20.777 tons of construction waste contaminated with DDT (**a total **of** 106.38 tons) was weighed and then incinerated in an environmentally safe manner in the HWI. Incineration of the DDT granulate was completed on **13 October 2008**. The total cost of the disposal measure was **EUR 268,000,** or EUR 2,519/ton.

5 Summary

Carrying out disposal measures for obsolete pesticides in developing countries requires primarily technical experience and country knowledge. With its Country Offices, good country knowledge and corresponding networking, GTZ is ideally suited to manage disposal measures. Cooperation between GTZ and disposers results in a symbiosis which makes implementation of complex disposal measures in developing countries relatively simple.
The main problem in this project was limited to logistics, starting with customs clearance at Dar Es Salaam and extending to the transport of the DDT to Germany.
The Old Korogwe project is a model project. Not only was this the first time that a pesticide store in a developing country had been completely demolished and the contaminated construction waste incinerated in an HWI in an OECD country, but also local NEMC personnel were trained during implementation of the disposal measures, enabling NEMC to carry out safety and disposal measures competently on its own for the other obsolete pesticide stocks in Tanzania. In Tanzania there are still some 300 stores with an estimated 1,200 tons of obsolete pesticides that need to be disposed of in the next few years.

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THE NATIONAL PROFILE ON CHEMICALS MANAGEMENT IN THE REPUBLIC OF MOLDOVA

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Abstract

The present paper refers to the National Profile on Chemicals Management in the Republic of Moldova (NP) which was developed within the project "Moldova-UNEP Partnership on capacity building for improving the environmentally sound management of chemicals in the Republic of Moldova and the implementation of the Strategic Approach to International Chemicals Management (SAICM)", implemented by Sustainable POPs Management office, the Ministry of Ecology and Natural Resources and the UNEP Chemicals Branch within the framework of the Quick Start Program. The purpose of NP was to evaluate the situation for chemicals management within the country and highlight the problems of their management during the entire life cycle. The elaboration of the NP lead to the achieved of such objectives as: integration of dispersed information on various subjects relating to the manufacture, import, export, use and disposal of chemicals; identification of legislative, institutional and technical gaps, reflecting ongoing and planned activities, assessment of problems in the country; initiation of a comprehensive and transparent process for elaboration of the national program and action plan in the field of chemicals management; strengthening of cooperation among all stakeholders, such as specialized central public administration authorities, the private sector and civil society, thus raising awareness and promoting exchange of information.

The NP findings and recommendations served as the basis for improving chemicals management at different national and international level and were taken into consideration during the elaboration of plans for socio-economic development of the country, such as the National Program on Chemicals Management in the Republic of Moldova and projects of technical assistance and investment in this sector.

Key-words: Chemicals management, assessment, life cycle, legislation, sustainable development, waste management.

How the NP was prepared

In order to ensure synergy while implementing international treaties on chemicals management, to which the country is a Party an Inter-ministerial Working Group was created with the purpose of supporting the elaboration of the NP. The process of NP development was coordinated by the SAICM project implementation team in cooperation with local and international experts. Thus, the NP was developed following meetings of the Task Team, workshops involving all concerned parties, discussions with stakeholders and affected parties, compilation of questionnaires and field visits.

NP Content and Findings

The Republic of Moldova is in transition to a market economy. Quick destruction of former soviet state economy after 1991 caused serious hardships to sustainable development of the Republic of Moldova. This process has involved initiation of restructuring and reform of institutions and economic activity and has been accompanied by a sudden decline of production in all sectors of national economy. Serious problems in all spheres of national economy have proceeded till now. The chemicals and waste management field, being a part of above-mentioned system, has never escaped the hardships.

The elaboration of the NP revealed that the Republic of Moldova produces a narrow range of chemicals, largely oriented towards the domestic market, namely pharmaceuticals, dyes, paints and varnishes, and perfumery products. Presently in the country, there are 187 enterprises specializing in the manufacture of rubber and plastic products and 69 chemicals industry enterprises (19 pharmaceutical and medicine factories, 12 factories producing soap, detergents, perfumery and cosmetic products, etc) [1]. As well the chemical substances are used in the manufacture of paper, in light industry, in the construction materials industry, in manufacture of food products, including wine, etc.

The volume of industrial production in 2007 constituted 2157,7 mil. U.S. dollars of which products of the chemical industry (medicines and pharmaceutical products, cosmetics and washing products, carbon dioxide and oxygen) contributed 29,5 mil U.S. dollars, which constituted only 1.4% of the total volume of industrial production [2]. Thus, with all the industrial production the impact of chemicals on the environment and human health persists, both from the emissions released by industrial activity, and accidents implicating chemicals during their transportation, use or storage, because of weather or technical conditions or a human factor .

The majority of the country's needs for chemical substances is covered by imports into the country, which in 2007 comprised 317.7 mil U.S. dollars (8.6%) were chemicals 414,0 mil. U.S. dollars (11,2%) were petroleum products [3]. The main chemical substances imported into the country were: petroleum products, fertilizers, pesticides, diverse raw materials, products and substances for the manufacturing industry and for other industries (e.g. re-export of mineral or chemical fertilizers containing two or three nutrients in the years 2003-2004 comprised about 15-20%, for the pesticides category this quantity (1-2%) is insignificant).

The overall management of chemicals in the country is divided between many sector specific ministries, including Ministry of Ecology and Natural Resources, Ministry of Health, Ministry of Agriculture and Food Industry, Ministry of Economy and Commerce, Ministry of Internal Affairs, a range of institutions such as Chamber of License, National Bureau of Statistics, Transport Agency and research institution within the Academy of Sciences of Moldova, etc. Although continued effective cooperation between above mentioned ministries will be necessary to ensure safe management of chemicals into the future, additional reorganizations to create an overall chemicals agenda for the country is seen as an important national advance. In this context, creation of a National Authority for chemicals management, for instance, should be considered with wide-ranging responsibilities and linkages to national development initiatives including chemicals governance, Millennium Development Goals and economic development of the Republic.

Current situation on the area reveals that while control of plant protection products and fertilizers including registration and compliance throughout parts of their lifecycle are reasonably controlled, the control of industrial chemicals is weak and more effective legislation is urgently required, such as the proposed the new Law on Chemicals with the goal of improvements of chemicals management and increasing the efficiency of control over emissions and impact of chemicals on environment and human health (currently being developed), plus there is need for adoption of a strong national compliance program.

During the visits carried out to enterprises during the period of elaboration of the NP (performed by the SAICM project PIU and national consultant) was revealed that labelling of chemicals imported/exported/re-packaged/ used etc. and drafting of the relevant material safety data sheet (SDS), are weak. Labels and SDS should stipulate the hazardous properties of the chemical, use signal words (danger, or warning), apply UN pictograms, stipulate emergency response measures, etc. in accordance with the international and EU standards. Adoption of such procedures is urgently required to protect human health and the environment from improper use from purchase through to disposal of the substance.

Another unresolved issue in chemical products with expired terms which are accumulated in the laboratories of academic institutions, at enterprises, etc. Compilation of data in the area of chemicals management is difficult as basic factual chemicals data is not available with sufficient provision, and the Republic of Moldova lacks the Chemical Substances Register (IT searchable data base) and no proven record of internal cooperation for exchange of data between ministries. These issues should be addressed in the near future so that the country's administrative arrangements are coordinated as industrialization and increased chemicalization of the country proceeds.

While the process of chemical importation, including involvement of the Chamber of License and relevant ministries approval (i.e. approval from the Ministry of Agriculture and Food Industry, Ministry of Ecology and Natural Resources, Ministry of Health, etc), has been adequate in the past, a review of importation requirements is urgently needed as the granted license does not cover the name of the chemical substance imported and its quantity. In addition there are many cross sectoral issues that need to be addressed in this regard.

Furthermore, the activities on raising awareness among governmental organization, industry and civil society involved in chemicals management and not only according to international treaties in the sphere of international chemicals management, including SAICM, European regulation REACH, International Conventions, is undertaken at a very low scale, essentially through the Moldova/UNEP Partnership on Capacity Building for Improving the Environmentally Sound Management of Chemicals in the Republic of Moldova and the Implementation of Strategic Approach to International Chemicals Management (SAICM) project activities.

Concerning the Industry and Private Sector there is week cooperation between chemical industry representatives with the central specialty public administration authorities, including SAICM project PIU. Thus, promotion of such activities as presentation of efficient solutions for solving environmental problems, adoption of International Chemical Industry's 'Responsible Care®' programs, workers awareness at work place, etc, orientation and directing industrial sector towards compliance with international requirements on classification and labelling of chemicals according GHS system, use of EU experience in implementation of REACH regulation remains partially undertaken or is lacking at all.

Lack of civil society awareness regarding the hazard associated with chemicals presents a challenge for national development and the reduction of risks associated with unsafe use of chemicals. Consequently, there is vital need for education programs for schools and civil society to be initiated and skills-building at universities and institutes to be strengthened to provide a skilled workforce for the expected industrialization of the country. Furthermore promotion of public access to environmental information, access to operational and monitoring databases of different ministries, diverse institutions, agents, universities and research centres. Civil society especially those involved in medical activities should be able to access relevant hazard data associated with chemicals, emergency-treatments and appropriate antidotes from a recognized poisons control centre, or similar organization.

Conclusions

Development of the NP has clearly illustrated a major need to increase the technical capacity of the country in order to be in a position to more effectively implement further chemicals management action plans and to be in an effective position to respond to the requirements of SAICM. While the selection of appropriate chemicals management measures is undoubtedly linked to a country's economic, social and cultural situation, government authorities need to consider chemical safety as a broad-sectoral issue involving all stakeholders. Without strengthening the national capacity and enhancing the knowledge and understanding of current stakeholders, Moldova will be at a disadvantage both internationally and during intensive EU Accession negotiations.

Thus currently, "Moldova-UNEP Partnership on capacity building for improving the environmentally sound management of chemicals in the Republic of Moldova and the implementation of the Strategic Approach to International Chemicals Management (SAICM)" is in the stage of finalisation of the Programme on sound management of chemicals (Programme hereinafter) which will focus on problematic areas of the sector, resulting from examination of current situation in this area and particularly stress in the NP. The programme is the main document of long term strategic planning, which determines the development objectives of the sound chemicals management system until 2020.

Therefore, the overall aim of the programme lies in developing an integrated system of chemicals management being efficient from the technical, economic, social and environmental points of view.

The objectives of chemicals management development at national level will include overall strategic objectives until the year 2020 for chemicals management and specific strategic objectives on medium term until 2015, inclusively for the management of priority chemicals.

The programme promotes a dynamic process of strategic planning in the field chemicals management, which shows the development directions, identifies the ways and mechanisms for achieving the general objectives, being implemented in two stages:

i. Stage 1: 2010-2015 - will focus on improving the legal, regulatory and institutional integrity for chemicals management, aligned to international standards, strengthening of human and technical capacities, initiation of activities to reduce risks associated with the priority hazardous chemicals.

ii. Stage 2: 2015-2020 - will focus on developing and implementing strategies for assessing and reducing risks associated with management of hazardous chemicals, cleaner production implementation, strengthening analytical capacity through the application of good laboratory practices.

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THE BIGGEST P.O.P. CLEANUP PROBLEM IN POLAND – "RUDNA GORA" INDUSTRIAL LANDFILL FOR HAZARDOUS WASTE

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Summary

The problem of the Rudna Gora pesticide waste landfill in Jaworzno was already mentioned during the previous 9th International HCH and Pesticide Forum in Chisinau, Moldova. Within the last two years, there has been a significant change in external factors, stemming out of the obligations of Poland as a party to the Stockholm Convention, and some real efforts have been made to get the problem resolved.

The Rudna Gora landfill formally belongs to the Organika-Azot Chemical Plant, which inherited it from the largest in socialist Poland, state-owned company engaged in production and retail packaging of pesticides. It is estimated that the landfill contains at least 160 000 tons of mixed waste, more than half of it being hazardous waste, including PPOs. The landfill is located in the basin of the Vistula River flowing into the Baltic Sea, hence it was placed on the list of "hot spots" drafted under the Stockholm Convention. Currently, the formal significance of the landfill has increased in the light of Poland ratifying the Stockholm Convention and as a result of expanding the list of PPOs covered by the Convention by additional 9 compounds. Three of them (lindane, α-HCH and β-HCH) were found in the landfill in large amounts.

Right now, the landfill is subject to systematic testing under the FOKS (Focus On Key Sources Of Environmental Risk) international programme, which is designed to finally determine its environmental risks and indicate practical ways of dealing with them. Also, the Plant Protection Institute – National Research Institute, Sosnicowice Branch is in charge of conducting random monitoring of the site.

The presentation includes estimated data on quantities of waste stored on the landfill, talks about the new factors resulting from the international conventions signed by Poland, describes hydrogeological conditions around the site and its impact on the environment (including selected test results) and explains the measures undertaken to resolve the problem.

Key words:

Pesticide waste, Rudna Gora landfill, POPs, remediation, water and soil contamination, leachate interception, removal of contaminants.

Introduction

Within the last two years, new circumstances arose which justify having yet another International HCH and Pesticides Forum presentation devoted to the topic of Poland's largest landfill storing pesticide waste. It is the Rudna Gora landfill in Jaworzno, a shameful remnant of past activities of the state-owned Organika-Azot Chemical Plant. The landfill is located in southern Poland, in the basin of the Vistula River, which is the major source of pollution for the waters of the Baltic Sea. (Fig. 1). Very close to the landfill runs the Wawolnica stream, which flows into the Przemsza River, which, in turn, is a tributary to the Vistula River.

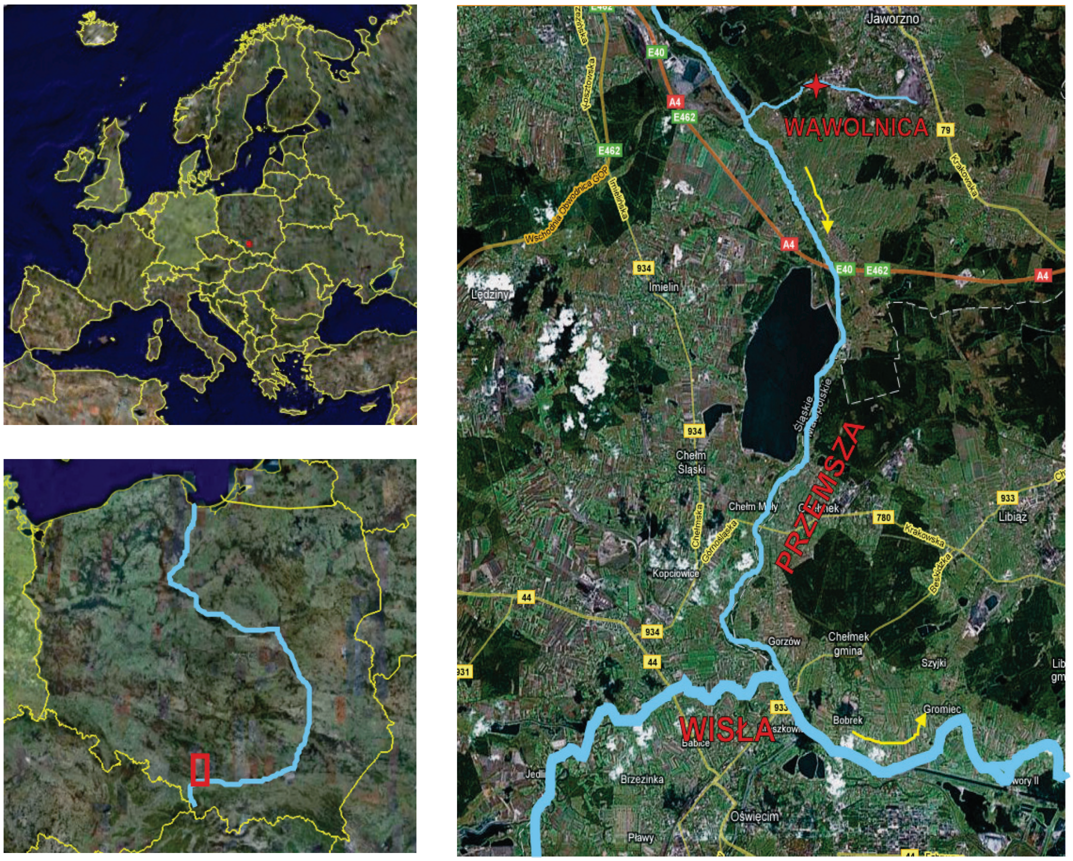

Fig.1 The location of the Rudna Gora Landfill

The land form around the site and its geological structure make the underground waters runoff flow toward the Przemsza River too, creating a potential way of transporting the contaminants. The landfill is located in a basin of a former sandpit quarry. The first, non-potable water-bearing level runs through pervious Quaternary sand formations. Those waters are directly exposed to contamination from the landfill leachates. Usable water resources, located in the deeper Triassic and Carboniferous formations are separated from the Quaternary waters with a layer of well compacted loams with a very low filtration coefficient. Studies performed so far indicate that there is no hydraulic connection between the water at the top water-bearing level and the usable waters in the lower Triassic and Carboniferous strata.

The landfill, now owned by the Organika-Azot Chemical Plant (a joint stock company owned entirely by the employees, formed in the process of conversion of a state-owned enterprise) is officially named Rudna Gora Central Waste Landfill, it takes up an area of 14 ha and is next to the so called "Field K", which covers an area of around 6 ha and belongs to the town of Jaworzno. „Field K” was mainly a landfill for municipal and mining waste, but it also stored cyanide waste coming from the Chemical Plant. Surface water from the field, diverted through drainage trenches, flows across the Rudna Gora Central Waste Landfill and connects to the trenches surrounding the landfill. The ownership structure does complicates the picture, but for technical reasons, both areas should be regarded jointly, as one and the same problem and one and the same facility, further referred to as the Rudna Gora Landfill.

The landfill contains a total of around 160 thousand tons of waste, including close to 88 thousand tons of hazardous waste, which contain, among others, persistent organic pollutants (POPs). Those include pesticide waste (DDT, HCB, dieldrin), scattered throughout the waste mass in the amount estimated to be around 30 tons, when converted into pure substance, lindane production waste, mainly α-HCH with some β-HCH and γ-HCH, in the amount estimated to be over 17 thousand tons of pure substance, as well as considerable amounts of waste, like salts and cyanide solutions (over 45 thousand tons), mercury waste (over 8 thousand tons) containers contaminated with hazardous waste (over 10 thousand tons) and other hazardous waste. The amounts are estimates only, due to lack of inventories of waste stored at the site.

At the north-east end, the landfill borders the vast premises of the Organika-Azot Chemical Plant, where the Wawolnica stream runs right through the middle. At various locations around the Plant, there were stashes of pesticide, cyanide and mercury waste, therefore the Plant itself is also a source of contamination spreading into the underground water and the Wawolnica stream, which carries them down toward the landfill.

Because of its location in the basin of the Vistula River, the landfill was placed on the list of “hot spots” drafted under the Helsinki Convention on the protection of Baltic Sea. It is also an important problem in the light of the Stockholm Convention on persistent organic pollutants.

New circumstances arising under the Stockholm Convention.

In the light of Poland’s obligations arising under the provisions of the Stockholm Convention, the situation of the Landfill has recently changed.

First of all, after several years of anticipation, Polish Parliament has agreed in the Act of 13.06.2008 that Poland's President can ratify the Stockholm Convention, which actually took place on 30.09.2008. The Stockholm Convention, which pursuant to its Art. 26, came into effect on 17.05.2004, started to apply to Poland 90 days after it was ratified, i.e. on 21.01.2009. Art. 26, section 2 of the Convention). Since that day, pursuant to Art. 6 of the Convention, Poland is formally obligated to take steps in order to reduce or eliminate releases from stockpiles and waste containing POPs.

Second, in 4-8 May, 2009, fourth session of the Conference of the Parties of the Stockholm Convention on Persistent Organic Pollutants was held in Geneva, where it was decided to expand the list of POPs by additional 9 substances. These include: chlordecone, hexabromobiphenyl, pentachlorobenzene, lindane (γ-HCH), alpha hexachlorocyclohexane (α-HCH), beta hexachlorocyclohexane (β-HCH), tetrabromodiphenyl ether and pentabromodiphenyl ether, hexabromodiphenyl ether and heptabromodiphenyl ether, also perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride. Three of them (α-HCH, β-HCH and γ-HCH) are present in large amounts at the landfill (total of 17 thousand tons when converted into pure substance), which makes the weight of the problem significantly heavier in the light of the Stockholm Convention.

The impact of the landfill on the environment in the light of most recent studies

The monitoring activities performed by the Organika-Azot Chemical Plant focused so far on collecting samples of the Quaternary underground waters, taken from a network of piezometers located throughout and around the landfill as well as testing the surface water (mainly the Wawolnica stream and the trenches surrounding the site). Independently, periodical testing of Wawolnica and Przemsza waters is performed by the National Inspection for Environmental Protection and random testing of water and bottom deposits of both Wawolnica and Przemsza is conducted by the Plant Protection Institute – National Research Institute, Sosnicowice Branch. The results of the testing indicate presence of a wide range of pesticides in the test material, but the top of the list includes HCH isomers, regularly occurring DDT and, in lesser amounts, chlorfenvinphos and tetradifon. A separate problem is posed by cyanides being released from "Field K". The results of the measurements vary over time and depend on the season, and the amount of precipitation, yet most of the measuring points show a steady decline of contamination. Highest concentrations of pesticides in

underground water, reaching 300 μg/l were observed in test holes located at the landfill, right next to the waste stockpiles. At the edge of the landfill, along the underground water flow (a well-studied strip going south west) concentrations of pesticides reach over a dozen μg/l.
Similar concentrations are found in surface waters, in the Wawolnica stream and the drainage trenches surrounding the landfill. Przemsza, below the confluence with Wawolnica had only trace amounts of pesticides. Random tests of the Wawolnica and Przemsza bottom deposits demonstrate very high concentrations of pesticides present in the bottom deposits of the Wawolnica stream, exceeding standards applicable to soils several times. Bottom deposits of the Przemsza River also show considerable amounts of pesticides, but particularly troubling are high amounts of lindane present in some of the samples.
It is clear that the scope of the monitoring at the site is quite substantial. Yet, some of the basic questions pertaining to potential threats posed by the landfill still remain unanswered:
1. Has there ever been any, even a trace contamination of the usable underground water resources pumped at several locations by the Municipal Water Supply and Sewage Treatment Company for the residents of the town of Jaworzno?
2. Are the Quaternary underground waters around the site, which are directly exposed to the contaminants in any hydraulic contact with the water in the Przemsza River and is there a treat that the contaminants could drain through the river toward the Baltic Sea?
3. How do the contaminants present in Quaternary underground waters spread and what is their current range?
Some important insights as to the above questions were obtained in 2008 and 2009, following a series of additional studies. First, in summer of 2008, the Plant Protection Institute – National Research Institute, Sosnicowice Branch performed testing of water samples collected from four different locations, which the town of Jaworzno uses as water intakes (three currently used intakes and one back-up). The tests covered 39 pesticide compounds and found no pesticides at either location. Potential contamination of municipal water supply also became a subject of a study conducted by Greenpeace, which at the beginning of 2009 independently collected samples from three currently used water intakes and had them tested by a laboratory in Exeter, UK. These tests also confirmed that the water supply used for Jaworzno residents is free of any pesticidal contamination.
In spring of 2009, Plant Protection Institute, National Research Institute, Sosnicowice Branch conducted a geological study in direct proximity to the Przemsza River, along the direction of underground water flowing away from the landfill. Data obtained from two new test holes and one existing piezometer showed the level of underground water is more than dozen centimeters below the bottom of the river, therefore there is probably no hydraulic connection between the Przemsza River and the underground waters (Przemsza does not drain the terrain and underground water does not get through to the river). This piece of information, which needs to be confirmed with studies performed during the different seasons throughout the year is very important considering the Helsinki Convention, because in this case, it would be sufficient to cut off the supply of contaminants coming into the Przemsza River via surface waters of the Wawolnica stream, to get the landfill removed from the list of sites that endanger the Baltic Sea. The studies also provided some insight as to the way in which the contaminants might spread in underground water. Samples of Quaternary underground waters (not used as municipal water supply) collected from the test holes and the existing piezometer, located around 1800 m away from the landfill show only trace amounts of some pesticides, which demonstrate that the landfill does not have a significant impact on the area at that distance.

Measures designed to resolve the problem.

Practical measures to cap the spread of contaminants from the landfill are limited to the efforts undertaken by its current owner, Organika-Azot Chemical Plant, using their own resources and within the confines of their budget. They were started when the company was undergoing restructuring and they have continued up till today. Beside the monitoring described above, the Plant dug a network of drainage trenches around the site, capturing much of the leachate from the landfill, built a leachate pumping station and provided a temporary cover over the major part of the landfill, the so called Pile, using inert material. In 2003-2004 the Plant modernized its production sewage treatment technology at its treatment station to remove pesticide contaminants via activated carbon bed. Recently, in 2009, the existing pumping station was modernized to intercept all leachates captured in the drainage trenches and direct them to the company's sewage treatment facility. For the leachate retention tank the company is using an emptied concrete pond, where it used to collect post-production waste silt. The work was completed in mid-2009. Now, all leachates intercepted from the landfill are treated and any sewage water dumped into the Wawolnica stream complies with applicable standards. The ongoing monitoring of Wawolnica should soon give us some indication as to whether these changes are effective.

Beside the above mentioned studies, the Plant provided funds for research on the hydrological conditions and contamination around the landfill. Independently, the town of Jaworzno also commissioned similar studies for the Field K. The information gathered so far is very valuable, yet it is still insufficient to decide on the next steps and what would be the best ultimate resolution of the problem. Under the initiative of the Central Institute of Mining in Katowice (project coordinator), collaborating with the Town of Jaworzno and the Plant, the parties engaged in the FOKS (**F**ocus **O**n **K**ey **S**ources) international research project, with most of the funding provided by the EU Regional Programme "Central Europe". This international programme is scheduled to be conducted in several pilot locations, including Germany, the Czech Republic, Poland (Jaworzno) and Italy. The project, designed to last three years (completion is expected in October of 2011), includes studies of underground and surface water contamination, as well as soil contamination, which would allow to locate waste storage places, trace the paths of contaminants migration, test out new disposal methods and eventually point to the optimal disposal technology for the site and estimate costs of such undertaking. The studies are to be comprehensive and include, besides the Rudna Gora landfill, the premises of the Organika-Azot Chemical Plant and some other identified sites storing hazardous waste within the town of Jaworzno.

In December of 2008, the Marshal of the Silesian Province, together with the President of the Town of Jaworzno and the Plant's Board submitted a written appeal to Prime Minister Donald Tusk for help to resolve the issue. The appeal is significant, since the President of Jaworzno declared his willingness to take over the landfill, which now belongs to the Plant. This declaration opens up a possibility of receiving public funding for the undertaking. So far, the fact that the Rudna Gora Central Waste Landfill was formally owned by the Plant prevented Polish government from committing any funds for the project, since current regulations ban the use of public funding for privately owned companies.

Summary

The results of the studies of water supply collected from currently used water intakes around the landfill, data from recent geological studies and the real efforts undertaken by the Chemical Plant, combined with the project designed to provide the ultimate solution to the landfill problem, allow for a more optimistic assessment of the situation than a year ago. Clearly, the site has not caused any irreversible environmental damage that would be a direct threat to people. It seems that if the FOKS research project is done right and in a timely manner and the time it takes to complete could be used to straighten out the issues of ownership of the site and open up the possibility of tapping into public resources for the project, the ultimate solution of the problem could be a question of a few more years. What is necessary, however, is strong government support in terms of financing and coordination of efforts.

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FOSTERING RUDNA GORA LANDFILL IN POLAND TO CREATE POSSIBILITIES FOR COST-EFFECTIVE AND SUSTAINABLE REHABILITATION

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Abstract

It is estimated that the *Rudna Gora* landfill in Poland contains at least 160,000 tons of mixed waste, of which more than half is hazardous waste, including POPs and HCHs. Located in the upper basin of the Vistula River Rudna Gora is a source of serious groundwater and surface water pollution by cyanides, pesticides, heavy metals and solvents. There is a sense of urgency involved with regard to its remediation and rehabilitation because of the risks involved. This paper concentrates on the options for the sustainable rehabilitation of Rudna Gora, eliminating imminent risks in a cost-effective way by introducing two new techniques: natural capping and controlled plume interception. These new techniques offer opportunities to convert Rudna Gora into a unique and attractive nature park and recreational area for the residents of the nearby Jaworzno town. This paper makes an appeal for fostering Rudna Gora with the ultimate goal to eliminate it from the list of 'hot spots' drafted for the Helsinki Convention.

Key-words

Rudna Gora, landfill, Pesticides, remediation, rehabilitation, sustainability, cost-effectiveness, natural capping, controlled plume interception

Introduction

The Rudna Gora landfill in the town of Jaworzno is a real, unresolved pollution problem with transborder implications (Stobiecki, 2007). The site is 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 is 20 ha in size and stores about 160,000 tons of waste, of which some 88,000 tons are classified as hazardous. The different types of waste cannot be separated, because the wastes are all mixed. The hazardous wastes are related to the synthesis of organochlorine insecticides in the adjacent chemical plant and include DDT, lindane, tetradifon and other pesticide active substances, breakdown products and post-synthesis waste (Stobiecki, 2007, Stobiecki, et al., 2007).
Currently, the formal significance of the landfill has increased in the light of the recent ratification by Poland of the Stockholm Convention and as a result of the expansion of the list of POPs covered by the Convention with an additional 9 compounds. Three of these (lindane, α-HCH and β-HCH) were detected in the landfill in significant amounts.

Setting

The Ruda Gora landfill is situated in the upper Vistula (Polish: Wisla; German: Weichsel) River catchment area. Its percolate groundwater and surface water are connected via the Wawolnica Stream and the Premsza Tributary to the Vistula River discharging some 475 km

to the north into the Baltic Sea (Bay of Gdansk). The middle and lower sections of the Vistula River are considered to be one of Europe's most exceptional areas of natural and landscape value, with meanders, ox-bows, steep banks and sand islands. These features form the habitats of 76% of the breeding bird species of Poland, including many species that are threatened in Europe. The most critical pollutants entering the Vistula River are: nutrients, phenols, heavy metals (Cd, Pb, Zn, Hg, Cu, As, Cr, Ni), plankton, organic compounds (Trihalomethanes, hydrocarbons and their derivatives, POPs, phenol compounds, pesticides etc.) and sediments (UNDP-DEWA, 2008). The Vistula River accounts for almost 70% of the pollutant load to the Baltic Sea (Buszewski et al., 2005).
From the available surface water and groundwater (percolation water) data from Rudna Gora (Stobiecki, et al., 2007) it can be concluded that Rudna Gora is a major contributor to the Vistula River pollution. To what extent Rudna Gora directly contributes to Baltic Sea pollution is still unclear, because of its long distance from the Baltic Sea, i.e. the dilution with Vistula tributary river waters downstream from Rudna Gora, the strong fixation of pesticides, metals and cyanides to the river sediments, and the constructed dams and barrages in the lower course of the Vistula River holding back the polluted sediments. However, pesticides, PCBs and other pollutants have been detected in the middle and lower reaches of the Vistula River as well, and in the Bay of Gdansk (Falandysz & Starndberg, 2004, Dimitruk et al., 2005). These pollutants should at least partly also be attributed to past use of pesticides and other now banned agro-chemicals on agricultural land, the residues of which still 'nourish' the groundwater and the surface waters.

Risk evaluation

Groundwater (percolation water) monitoring data as well as surface water monitoring directly around and downgradient of Rudna Gora show serious contamination with pesticides (HCHs, DDTs, DDEs and DDDs), heavy metals, cyanides and solvents. Identified risk elements are:
1. Risk of drinking water pollution: Jaworzno Town located directly upgradient of Rudna Gora, abstracts drinking water from two aquifers, respectively in Trias limestone and Carboniferous sandstone. It appears that these drinking water wells have not been polluted. It is unclear what future threat the drinking water wells of this town would pose, e.g. in case of increase of abstracted volumes.
2. Human and animal exposure risks: The Rudna Gora landfill has free access and is not fenced or secured, although part of the landfill has a surface cover of soil and debris. Surface run-off is partly intercepted with open drainage ways. Apart from the possibility of direct exposure to humans with the hazardous wastes stored, browsing animals (e.g. rodents) come into contact with the pollutants and are responsible for further spreading in the food chain.
3. Ecological risks: No pumping system has been installed for the hydrological control of Rudna Gora landfill and no continuous, effective surface protective cap is present. This leads to a situation of relatively free percolation of rainwater through the landfill and hence contaminant spreading into the environment, as demonstrated by the groundwater and surface water monitoring data. Overall contaminant levels in the percolation waters have decreased from 1996 onwards, but contaminant levels are still high today. This threatens the ecosystem and valuable habitats further downstream as indicated above.

Sustainable options for rehabilitation

From the available data it can be concluded that there is a sense of urgency for the remediation and rehabilitation of the Rudna Gora landfill to curb the imminent risks. For rehabilitating the landfill different options exist. These range from traditional options, i.e.

capping with a geo-membrane and/or surface clayey layer supplemented with hydrological control and percolate treatment, to state-of-the-art sustainable and cost-effective solutions. In this paper we concentrate on two sustainable rehabilitation options that were recently applied elsewhere, as follows:

1. Natural capping
2. Controlled plume interception

Natural capping

Since 2001, Tauw in a consortium with Witteveen+Bos Consultants is involved in the rehabilitation of the former landfill 'Volgermeerpolder', commissioned by the Municipality of Amsterdam, Netherlands. With a budget of EUR 100 Mio 'Volgermeerpolder' project is one of the biggest soil remediation and landfill rehabilitation projects currently ongoing in The Netherlands and Europe.

The Volgermeer consists of an area of about 105 ha just north of Amsterdam and was used as a landfill for domestic and industrial waste during the last century. Large amounts of chemical waste (including 30,000 drums of pesticide production waste) were dumped here during the 1960s and 1970s. A remediation and rehabilitation plan was prepared in the 1990s. Landfill rehabilitation is now in the implementation stage.

The whole Volgermeer will be capped with soil originating from ground works in the region. This soil will be covered with a HDPE foil. The foil makes the cap impermeable. HDPE was chosen because of recent developments in this technology and because of economic reasons. For the surface layer on top of the foil an 'ecological' option was chosen consisting of a wet cover coined as 'sawa' system ('sawa' is Indonesian for a bunded wetland rice field). The sawa system is currently being constructed in an area of 55 ha (Figure 1). The system consists of clusters of sealed compartments, separated by dikes which are filled with water and permits the development of aquatic flora and fauna (Figure 2). The sawa system acts as a biological filter for percolate and drainage water whilst also enhancing peat development.

The body of waste is embedded in an impermeable natural peat layer. Therefore percolation of contaminants to the deeper groundwater and laterally through the peat has not taken place, at least not in the past 30 years (and is not expected in the coming years), as demonstrated by the monitoring results of the shallow and deep groundwater around the site.

Because of the proven safe containment of toxic waste in the peat, the sawa system will also be used to develop a natural impermeable peat cap to ensure a much longer lifespan of effective capping than can be done by HDPE foil alone. This method is expected to be cost saving (many millions of Euros with time) and easy to install. As long as the organic (peat) layer is intact the isolation of waste will be secured. The Volgermeer will become an attractive location for science students and naturalists studying the peat formation in the sawas. Together with the Centre for Wetland Ecology (established by several Dutch universities), a number of programs are initiated to study the growth of peat and to assess the effects on the quality of the capping (isolation) of the waste.

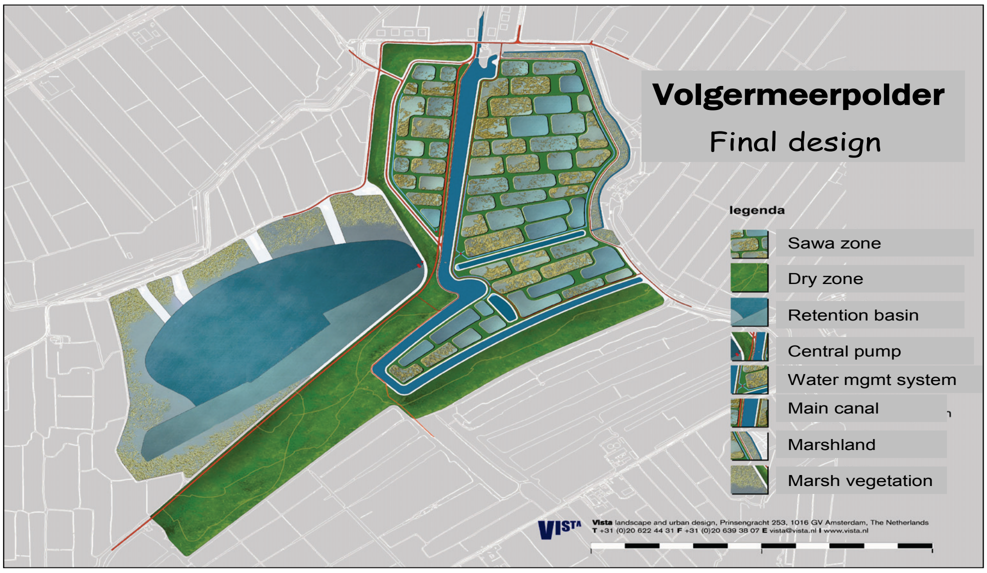

Figure 1. Volgermeer final design showing the sawa system

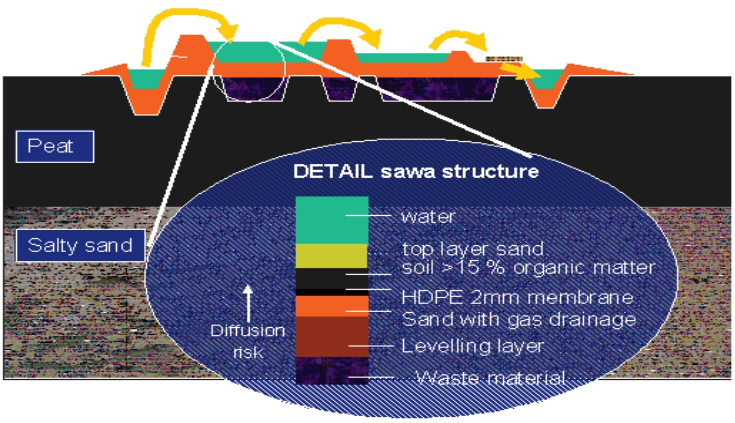

Figure 2. Cross section of the sawa system

Considering the types of waste stored, the Volgermeer is very well comparable with Rudna Gora. In spite of the Volgermeer being much bigger in size than Rudna Gora and the substrate hydrogeology being very different, we believe natural capping is an interesting option for Rudna Gora, for cost reasons and because of the opportunities for converting Rudna Gora into a unique and attractive nature park and recreational area for the Jaworzno town residents.

Controlled plume interception

The Volgermeer concept has revealed the unique characteristics of peat as an organic barrier to pollution. The characteristics of peat as effective contaminant filter can be used for landfills without (effective) impermeable bottom layer, such as Rudna Gora. After careful delineation of the percolate plume, specific locations are chosen where the plume is intercepted. This is done by excavating interception ditches and pump installation (running on wind energy if possible), thus creating a hydraulic head. In this way the plume is halted and controlled. Inside the ditches natural peat blocks are positioned for filtering after which the treated water

is led to a natural stream. Currently this system is being installed at the Kanaalpolder rehabilitation project in the Province of Zeeland, Netherlands.
An important consideration is that artificial surface capping of former landfills is never waterproof and will get damaged after all. Many lessons were learned in this respect over the last 10 years by leak detection surveys on geo-membranes (Van der Wijk et al., 2008). In other words, some form of percolation plume control will always be necessary, also in case of surface capping with foil. This method controls and treats the plume in a cost effective and natural way, whilst minimizing downgradient environmental damage.

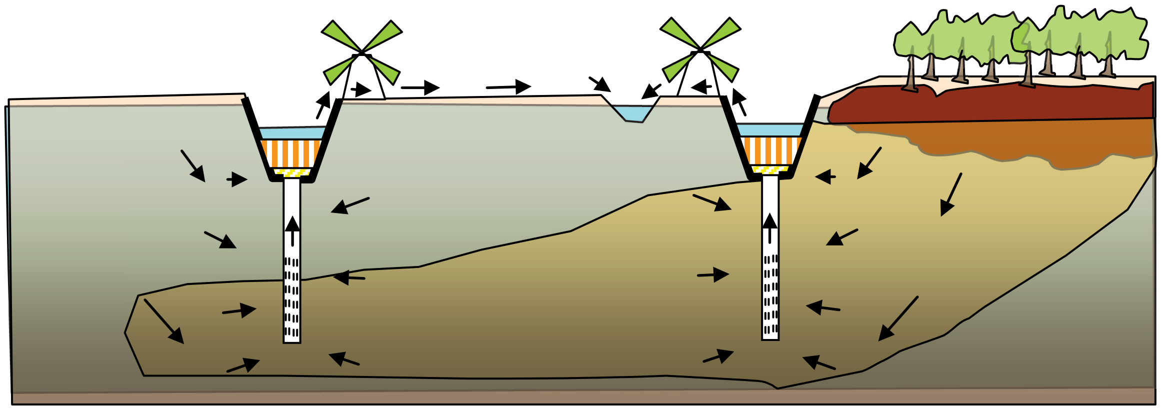

Figure 3. Cross section controlled plume interception

Selection of sustainable rehabilitation options

To arrive at a sustainable cost-effective rehabilitation plan for Rudna Gora, we suggest to use the REC decision support system, selecting the most appropriate option. This is done by comparing for each option the Risk reduction achieved (R), the Environmental merits (E) and the Costs (C). The rehabilitation option that reduces the risks below acceptable limits, whilst providing the most environmental merits at the lowest cost will subsequently be developed in detail.
The options to be assessed can in principle be defined by using the two techniques described above, or adaptations or combinations of these.

Conclusion and way forward

After studying the information available sofar on Rudna Gora landfill, we conclude that there is a sense of urgency with regard to its remediation. There are good possibilities for sustainable and cost-effective state-of-the-art remediation and rehabilitation options as explained above. Rudna Gora's rehabilitation is potentially viable and technically feasible.
The way forward can be outlined in three steps as follows:
A. Initial study: 'unlock' available information, most of which is currently in Polish language; scrutinize and collate all information; also, find out more about the legal and social context of Rudna Gora; identify all stakeholders and their interests; inventory current initiatives, such as the ongoing FOKS (Study On Key Sources of Environmental Risk).
B. Fostering: identify one of more international organisations that would want to adopt the Rudna Gora pollution problem by assuming responsibility over Rudna Gora's rehabilitation, together and in close cooperation with the Polish authorities, either at the municipal, regional or national level; mobilize Polish authorities and secure manpower and funding.

C. Action plan: define a comprehensive set of sequential projects from environmental impact analysis to implementation, each which specific terms of reference; tender these projects.

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IN-PILE THERMAL TREATMENT OF DIOXIN CONTAMINATED SOIL AND SEDIMENTS

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ABSTRACT: Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs, or more simply, dioxins) are known human carcinogens. Dioxins are formed as by-products in the manufacture of organochlorides, in the incineration of chlorine-containing substances such as PVC (polyvinyl chloride), in the bleaching of paper, and from natural sources such as forest fires. There have been many incidents of dioxin pollution resulting from industrial emissions and accidents; the earliest known incidents having occurred in the mid-18th century. Releases of dioxins related to industrial activity are known to have occurred in many countries.

Environmental restoration of dioxin-impacted sites has typically involved removal of impacted soils ands sediments, with either containment in a chemical disposal facility or incineration. Dioxins decompose at temperature ranges as low as 300 to 400°C in oxygen-deficient conditions (Behnisch et al. 2002). The authors are in the process of evaluating a number of sites in the U.S. for the application of TerraTherm's In-Pile Thermal Desorption (IPTD) process as a means of performing onsite thermal decomposition of dioxins. The benefits of on site treatment are no off-site transport costs, elimination of potential vehicular accidents associated with offsite transport and disposal, no long term liability, and unlimited onsite use of the impacted soils and/or sediment after treatment.

TerraTherm's preliminary designs for a site in Rhode Island call for a series of treatment cells, each having a capacity of approximately 575 m^3, with a treatment time of 45 days. The treatment cells would be heated under negative pressure, to a minimum target temperature of 325°C. Multiple treatment cells allow for the sequencing of treatment such that some are in operation while others are being constructed and others are in a cool-down mode and being sampled to confirm cleanup.

INTRODUCTION

Polychlorinated dibenzodioxins and furans (PCDD/Fs), are commonly referred to as dioxins for simplicity in scientific publications because every PCDD molecule contains a dioxin skeletal structure. The word "dioxins" may also refer to a similar but unrelated compound, the polychlorinated dibenzofurans (PCDFs) of like environmental importance. Typically, the *p*-dioxin skeleton is at the core of a PCDD molecule, giving the molecule a dibenzo-*p*-dioxin two-ring system. Members of the PCDD/F family have been shown to bioaccumulate in humans and wildlife due to their lipophilic properties, and are known teratogens, mutagens, and human carcinogens frequently associated with soft-tissue sarcoma, non-Hodgkin's lymphoma, Hodgkin's disease and chronic lymphocytic leukemia.

There have been many incidents of dioxin pollution resulting from industrial emissions and accidents; the earliest such incidents being in the mid-18th century during the Industrial Revolution. Industrial sources common in the 20th century included manufacture of organochlorine chemicals, including polychlorinated biphenyls (PCBs), pesticides such as pentachlorophenol (PCP), dieldrin and chlordane, and herbicides/defoliants such as Agent Orange (2,4,5-T). Dioxin was a by-product of the manufacture of these compounds, and therefore tends to be found at sites where these compounds were manufactured, used or disposed. According to the most recent US EPA data, the major current sources of dioxins are:

- Coal fired utilities
- Municipal waste incinerators
- Metal smelting
- Diesel trucks
- Land application of sewage sludge
- Burning treated wood
- Trash burn barrels

These sources combined account for nearly 80% of current dioxin emissions.

THE ISTD/IPTD PROCESS

Thermal conductive heating (TCH) refers to the application of heat to the subsurface through conductive heat transfer. The source of heat is typically from thermal elements, which can be oriented both vertically and horizontally. TCH in combination with application of negative pressure (vacuum), as practiced by TerraTherm, Inc. is given the commercial name of In Situ Thermal Desorption (ISTD), also referred to as In Situ Thermal Destruction. ISTD can be used to remediate soils contaminated with a wide range of organic compounds. When applied ex situ for treatment of excavated soil or sediment, this technology is termed In-Pile Thermal Desorption (IPTD). ISTD and IPTD are protected by over 25 U.S. Patents, numerous international patents and Patents Pending. IPTD in particular is covered by one or more of the following U.S. Patents: 6,881,009; 7,004,678; and 7,534,926.

Figure 1 shows vapor pressures versus temperatures for a variety of environmental contaminants and in situ thermal remediation technologies. Because heat and vacuum are applied simultaneously over a period of time, compounds having relatively low vapor pressures at ambient temperatures can be thoroughly removed or destroyed in situ (e.g., by pyrolysis) using this technology.

Heat and vacuum are applied simultaneously to the target media with an array of vertical or horizontal heater elements. For the ISTD/IPTD technology, each heater contains a heating element (typically electrically powered resistance heaters), with an operating temperature of approximately ~750 to 800°C. As the soil is heated, volatile, semi-volatile and non-volatile organic contaminants in the soil are vaporized and/or destroyed by a number of mechanisms, including evaporation, steam distillation, boiling, oxidation and pyrolysis (chemical decomposition in the absence of oxygen).

The vaporized water and contaminants, as well as some volatilized inorganic compounds, are drawn counter-current to the heat flow into the vacuum extraction wells (termed “heater-vacuum” wells).

Figure 2 provides a picture of a heating element that is encased in the heater well (lower) and the heater well completion (upper) at the surface.

Heat flows through the soil from the heating elements primarily by thermal conduction. As illustrated in Figure 3 the target temperature is the temperature that is maintained between the heater wells; the temperature immediately surrounding the heating wells is illustrated to range between 300 to 400°C, but can be as high as 500 to 700°C.

With the soils under vacuum, desorbed contaminants are drawn through the higher temperature zones immediately surrounding the heater-vacuum wells, where in-situ destruction reactions occur at high rates (Baker and Kuhlman, 2002).

As with ISTD, the IPTD process utilizes conductive heating and vapor recovery to remediate excavated soil and/or sediment contaminated with semi-volatile organic compounds (SVOCs), such as dioxins. Heat and vacuum are applied simultaneously to the soil piles or treatment cells with an array of horizontal heaters and vapor collectors.

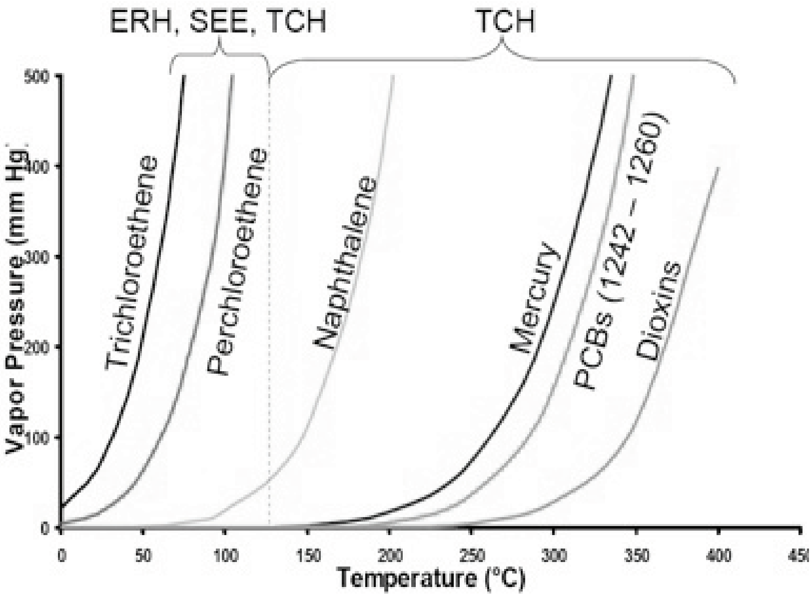
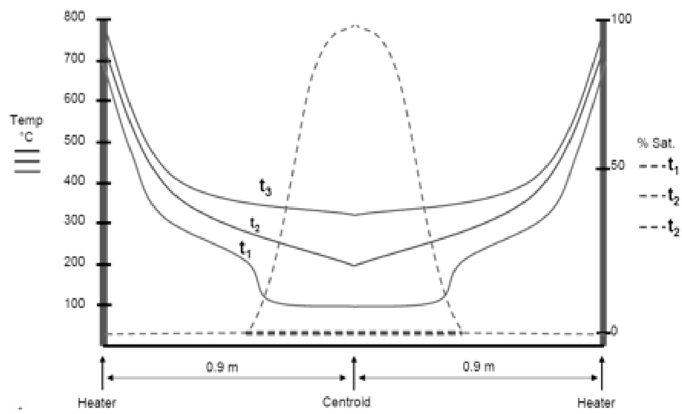


Figure 1:
Vapor pressures versus temperatures and environmental contaminants that can be treated using thermal methods. ERH = electrical resistance heating; SER = steam enhanced recovery; and TCH = thermal conductive heating.

In a typical IPTD installation for soils or sediments contaminated with high-boiling point semi-volatile organic compounds (SVOCs), such as dioxins, the coolest soil in between the heaters is heated to a target treatment temperature of 325°C. Based on various field studies, regardless of the type of contaminant of concern (COC), most (e.g., >95-99% or more) of the SVOCs are destroyed as they pass through the superheated soil in proximity to the heater-vacuum wells, before they arrive at the extraction wells (Stegemeier and Vinegar, 2001; Baker and LaChance, 2003).



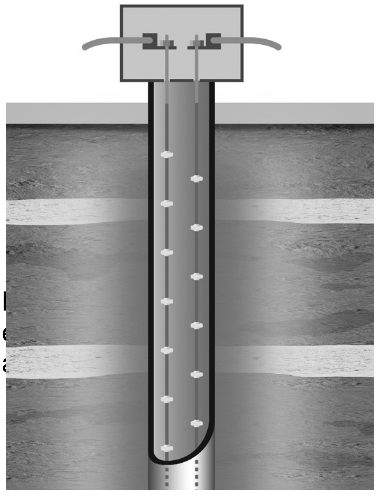


Figure 3: Temperature distribution between heater wells. The curves indicate the progression of heating up to the 325°C target temperature for dioxin-contaminated soil or sediment. *N.B.:* Time step 1 (t_1) depicts the heating process already underway, with locations between heater wells already up to the boiling point of water but still moist. Time step 3 (t_3) shows attainment of target treatment temperature at the centroid, with all water having been boiled off.

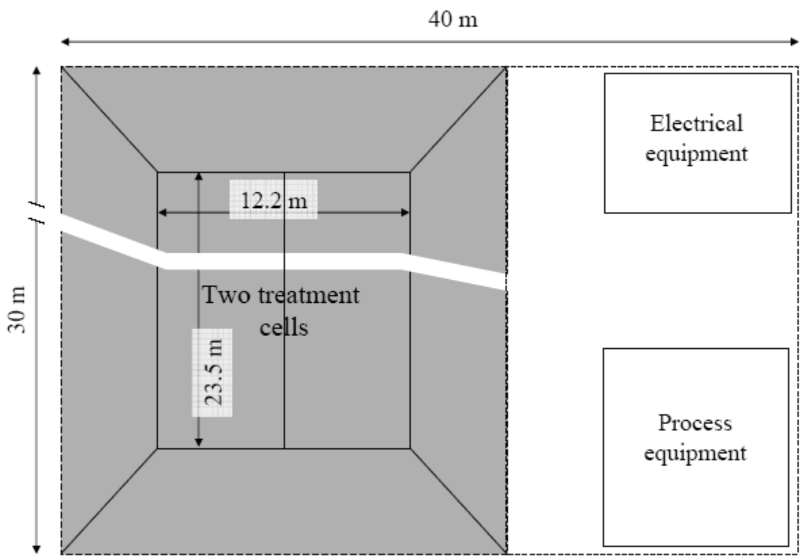


Figure 4: Sketch of the In-Pile Thermal Desorption (IPTD) Layout for Subject Site. The dimensions reflect adjacent treatment cells, each with volume of 575 m^3. Note that some additional space is required around the cells, as shown, to allow for installation, maintenance, and interim sampling.

PRELIMINARY DESIGN FOR THE RHODE ISLAND SITE

An IPTD design was developed to treat contaminated sediment in cells containing approximately 575 m^3 each. Multiple adjacent treatment cells would be constructed and utilized simultaneously. Design features include:

- A base pad that is both vapor-and liquid-tight.
- A leachate collection system, such as with a collection pipe installed in a trough running down the center of each treatment cell, or with a catch basin.
- Thermocouple ports installed through the surface cover and/or running laterally through the side walls at select locations to enable tracking of heating progress.
- Rigid sidewalls, with insulating panels to reduce heat losses during treatment.
- Heater elements and vapor injection and extraction wells distributed throughout each treatment cell.

• A soft insulating vapor cap used to contain fugitive emissions and allow for application of a net vacuum to each treatment cell.

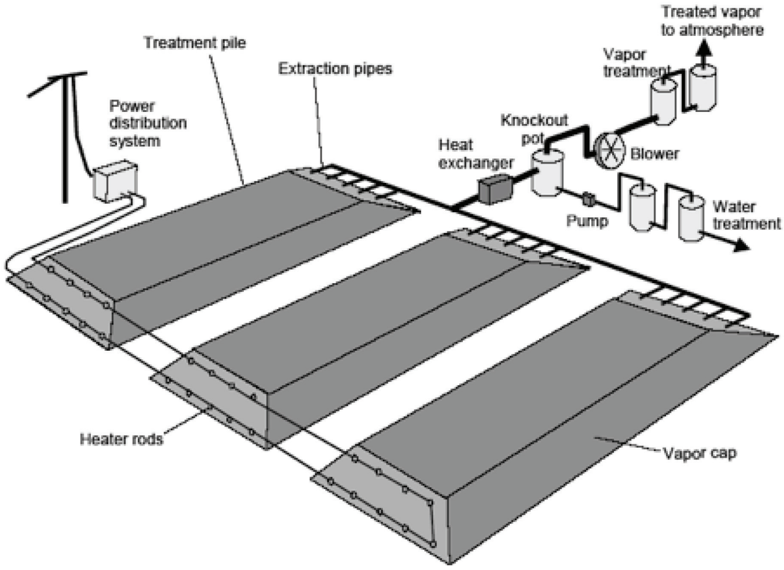


Figure 5: IPTD Construction Schematic. Heaters, air inlet wells, and vapor recovery wells are indicated.

SUMMARY

Remediation of dioxin-, furan- and PCB-contaminated soils and sediment has been limited (depending on concentration) to excavation and disposal in chemical disposal facilities, permitted landfills or incineration. Regulatory agencies have been stipulating very low cleanup criteria, requiring in many cases high-temperature incineration, which is very expensive. When utilizing ISTD / IPTD technologies, by contrast, destruction of these compounds through thermal decomposition occurs at temperatures at or about 325°C, with treatment taking place over a typical period of 45 days. This results in better than 99% reduction in concentrations, which in turn can result in unlimited soil use after treatment.

There are a limited number of incineration facilities in North America, involving long distance trucking of contaminated soils and sediments for treatment. According to the Center for Transportation Research and Education, at Iowa State University, the U.S. national trucking accident rate is 2.04/million miles driven. Long distance trucking of hundreds of truckloads of contaminated soils results in high probabilities of vehicular accidents involving toxic payloads.

Long distance trucking of soils and sediment for incineration also increases the carbon footprint for the project and as noted above the burning of diesel fuel can also result in the formation of dioxin. The IPTD technology represents a cost-competitive means of remediation of dioxin contaminated sites without the adverse impacts associated with current approaches.

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HARMFUL PESTICIDES CLEANED UP IN THE REPUBLIC OF MOLDOVA

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Abstract. The total amount of harmful pesticides in the Republic of Moldova was estimated at 7,245 tons, including about 4,000 tons buried at a pesticides dump in the southern part of country and 3,245 tons has been scattered in 424 poorly equipped or unfitted facilities, which lack proper monitoring and security.

As part of the Partnership Action Plan between Republic of Moldova and NATO and other part through Environmental and Security Initiative for Eastern Europe, NATO in collaboration with other international organization (the United Nations Environment Programme, the United Nations Development Programme and the Organization for Security and Co-operation in Europe (OSCE)) helps Moldova achieve its objectives in the filed of environmental security and its particular in the clean-up and destruction of hazardous chemicals on its territory and assisting Moldova in meeting its obligations under the international Conventions, Agreements and protocols.

Besides repacking of 3,245 tons in 37 safe storages with collaborative efforts by Government of the Republic of Moldova, NATO Partnership Trust Fund and OSCE, under the NATO Science for Peace and Security Programme (NATO SPSP) supported the establishment of a laboratory with sophisticated equipment and necessary training to analysis the pesticides, catalogue the dump sites and set standardized sampling procedures. Up to April 2009, more than 4800 samples of pesticides were tested and an overview of the nature of the pesticides stockpiles was obtained. To support Government objectives in the wine exportation in Russia and Belarus, the NATO laboratory certified wine to be pesticides fee. In parallel with the NATO Project, French company TREDI, with support of the Global Environmental Facility and the World Bank, incinerated around 1,200 tons of pesticides, using database of the chemical's composition and toxicological evaluation obtained by NATO laboratory.

Within framework of NATO SPSP, since 01 February 2009 has been started a study of the dispersal and mobility of harmful pesticides in the environment near to landfill, where has been buried more that 4,000 tons of pesticides during `70 - `80.

Key-words: harmful pesticides, NATO, OSCE, Ministry of Defence of the Republic of Moldova, repacking process, pesticides analysis, wine's export certification, database of stockpile's nature, environmental monitoring.

Background

Actually, the Republic of Moldova has an estimated 5,949[3] tons of harmful pesticides and dangerous chemicals: 1,949 tons of pesticides, which remain scattered in 22 central

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[1] Until year 2008, the quantity of harmful pesticides was 7,245 tons of pesticides. 1,296 tons were disposed in the Global Ecological Fund/World Bank Project "Management and disposal of the POPs stockpiles" by the French Company TREDI.

warehouses and 4,000 tons, are buried in the dump pesticides site in the southern part of Moldova.

Life expectancy at birth in Moldova shows patterns similar to the ones observed in neighboring countries and in some Eastern Europe countries. Although the decrease of this indicator has been reversed and presently it constitutes 68,4 years, it continues to register values much lower than the average for the EU states[4]. The RoM has made considerable progress in the area of essential health indicators, such as decrease of the infant mortality and maternal mortality rates. Over the period 2001-2006, infant mortality has decreased by 26% (from 16.3 deaths per 1000 new-borns in 2001 – to about 11.8 deaths per 1000 new-borns in 2006). The maternal mortality rate is now 16.0 maternal deaths per 100000 live births as compared to 43.9 in 2001. However, these indicators are still higher than the average European figures.

The mortality of the economically active population is higher than in the EU countries. The most important death causes in the RoM include diseases of the circulatory system, poisonings, malignant neoplasm, cancers and diseases of the of the liver, gallbladder and pancreas. But more frequently illnesses for economically active population are registered such as allergy diseases, digestive tract diseases, inflammatory diseases of skin and subcutaneous tissue (dermatitis, eczema, etc.) and others.

What is done? Concrete actions in diminishing the impact of obsolete pesticides' stocks in Moldova started in 2002, when *Ministry of Defence of the Republic of Moldova has been nominated as responsible institution for implementing of the prohibited and unused pesticides disposal programs in Moldova*[5].

As a part of Moldovan Individual Partnership Action Plan (IPAP) with NATO, Moldova is committed to work with NATO in the field of environmental security and in the clean-up and destruction of hazardous chemicals on its territory. To that effect, collaboration with NATO was officially launched in November 2006, at the initiative of the President of the Republic of Moldova. Embedde in the Environment and Security (ENVSEC) Initiative for eastern Europe NATO is collaborating with other international organization (the United Nations Environment Programme, the United Nations Development Programme and the Organization for security and Co-operation in Europe) to help Moldova achieve its objectives in the safe destruction of its chemical hazards and assisting Moldova in meeting its obligations under the international Conventions, Agreements and protocols.

The process of *repacking of **3,245**[6] **tons** of pesticides and dangerous chemicals* from 424 poorly equipped/demolished places/warehouses and safe storage in the 37 centralized facilities was completed in June 2008, with collaborative efforts by the Moldavian State Budget and the National Ecological Fund (430,000 EURO), NATO/Partnership for Peace Trust Fund – OSCE/ENVSEC (658,000 EURO, including the Dutch NGO MILIEUKONTAKT (150,000 EURO)). Map 1 shows the general status of the repacking and disposed of the harmful pesticides in dependence of the kind of the financial sources.

Actually status showed, that from totally amount of 1,949 tons of pesticides, 1,296 tons of pesticides are repacked in the UN/ADR package, and 653 tons – in Non UN/ADR package.

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[2] Government Decision No.1471 of 24 December 2007 on approval of the Healthcare System Development Strategy for the period 2008-2017.

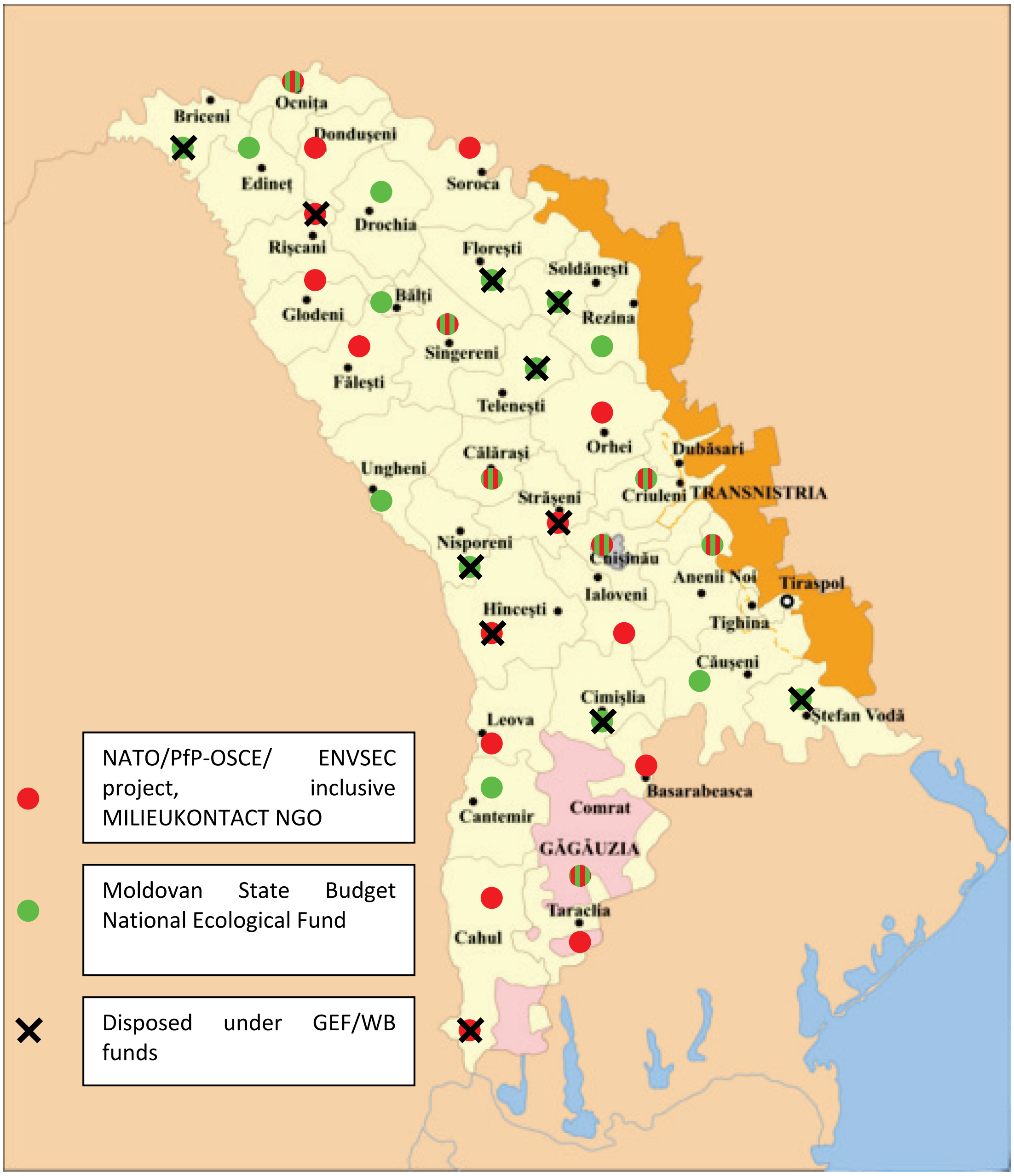
[3] Government Decision No.1543 of 29 November 2002 regarding additional measures for centralizing storage and disposal of prohibited and unused pesticides.

[4] Including 258 tons of pesticides, which were found buried/after fire/stocked in the discovered places, in accordance with Government Decision No.1217-525 of 12 November 2007.

	UN/ADR Package	Non UN/ADR Package	Total
NATO/PfP-OSCE/ENVSEC Trust Fund	1,269	309	**1578**
Other sources	27	344	**371**
Total	**1,296**	**653**	**1,949**

Since 2003 year, in the project's activities were involved more than 720 military personnel and 35 military techniques from NBC units of the National Army of the Republic of Moldova.

Map 1. The general status of the harmful pesticides activities



Besides repackaging and safe storage of the harmful pesticides, with support of the *NATO Science for Peace and Security Project "Clean-up chemicals - Moldova" (298,000 EURO)*, were established the analytical laboratory with sophisticated equipment for systematic characterization and analysis of the pesticides stockpiles, based on gas chromatography-mass spectrometry (GC-MS), high pressure liquid chromatography (HPLC), thin layer chromatography (TLC) and ion selective electrode (ISE). A NATO-funded laboratory is located at the State Centre for Certification and Registration of Phyto-Sanitary Means and Fertilizers in Chisinau. The project employs specialized personnel from Ministry of Defence of the Republic of Moldova for sampling and general project management and specialist scientists in the “phytosanitary products and fertilizers” of the Ministry of Agriculture for the laboratory activities. In addition, the Moldavian State University participates with specialists in analytical chemistry including a number of young scientists with general scope on training a new generation of scientists, that will be involved in the future in the Republic of Moldova for the pesticides issues. All personnel became operationally in standard sampling, analysis and data management techniques.

By the end of July 2009, an overview was obtained of the nature and composition of 3,245 tons of harmful pesticides stored in 2 municipalities, 32 districts of Republic of Moldova and the Territorial Autonomy Gagauzia. A total of 5,000 samples were tested by GC-MS, HPLC, TLC and ISE methods of analysis, which provided the identification in cca 87% of samples.

More than 70 active ingredients and their metabolites were detected. Among the identified compounds 49 of them have been prohibited or restricted for use in agriculture, in Moldova since 1970, while the use of 24 substances was prohibited or restricted in the UE countries.

The project’s benefits. In parallel with the NATO/PfP-OSCE/ENVSEC project, 1296 tons of the chemicals were incinerated by the French company TREDI, with the support of World Bank and Global Ecological Fund, using a database of the harmful pesticide’s composition and toxicological evaluation from Science for Peace and Security-funded laboratory to optimize the processes.

The laboratory was also equipped with sophisticated equipment test agricultural products for contamination, in order to enhance food security in the country. Therefore, this laboratory has been contributed to an economic upturn for the wine industry of Moldova. Wine growing and winemaking are major branches of economy of the Republic of Moldova. The country has a well established wine industry with 142 grape processing enterprises and a vineyard area of 147,000 hectares of which 102,500 ha are used for commercial production. The wine industry processes about 350-500 thousand ton of grapes each year. Most of the country’s wine production is for export (in 2008 – the wine was imported by 25 countries, such as Russia, Belarus, Ukraine, Kazakhstan, Poland, Canada, North Korea, Turkmenistan, Georgia, Belgium, etc. In October 2007, Russia, Belarus and Ukraine recommenced importation of Moldavian wine after more than 800 samples of wine from 35 companies were certified by the lab to be pesticide-free. Starting from December 2008, the project assists the Government of the Republic of Moldova in the task to export apples to Russia through the determination of pesticides residues in apple. The Moldovan wine and apple companies pay for to have the analysis carried out, and the proceeds from this activity will be used to obtain more equipment that is essential for future expansion of the laboratory’s activity.

Since May 2008, the project has been focused attention on the feasibility study of the dispersal and mobility of the harmful pesticides in the environment, away from the biggest dump site from s.Cismichioi, Territorial Autonomy of Gagauzia, near to Ukrainian and Romanian border, where 4,000 tons of pesticides have been buried in the early 1980s. The site is located close to watersheds discharging in the Prut river and the Dniester river.

Future objectives

1. Regarding the disposal of the 1,949 tons of harmful pesticides, Ministry of Defence in cooperation with NATO/NAMSA is identified the financial sources to accumulate 4 mln EURO in the NATO/PfP-OSCE/ENVSEC TRUST Fund. Taking into account the existing situation regarding the environmental, health and socio-economic risks associated with harmful pesticides dissipation and their local cost maintenance, the Government of Moldova is committed within mentioned fund with an amount of 500,000 EURO. Planned period – 2009 – 2011.

2. Within framework of NATO Science for Peace and Security Programme, Government of Moldova intends to implement a new project (2010-2012) entitled „Persistent organic pollutants pesticides impact on human health, environment and food". The MoD will be a local coordination point in coordination with Ministry of Health, Ministry of Agriculture and Food Industry, Ministry of Ecology and Natural Resources.

Conclusion

Ministry of Defence of the Republic of Moldova is open to co-operate with international organisations, states, NGOs, etc. in the environmental issues as well as defence against terrorism and countering other threats to security, which are perceived to treaten security, social stability and peace, human health and suitanaible development not only at local level, but at the entire Eastern Europe Region.

Acknowledements

Thanks go to the Environmental Security Iniative members and countries, in special to North Atlantic Alliance (the PASP, SPSP, NAMSA, etc.), that have permanently contributed and supported Moldovan iniatives in the clean-up and disposal of harmful pesticides and other hazardous chemicals.

BANGLADESH REPLACED PERSISTENT ORGANIC POLLUTANTS PESTICIDES (?) BUT YET TO GET RID OF DDT STOCKPILES

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Bangladesh, which has come a Party to the Stockholm Convention after ratification on 12.03.2007, deregistered and subsequently banned import, formulations and usage of 5 persistent organic pollutants (POPs) pesticides such as Chlordane, Aldrin, Dieldrin, Heptachlor and BHC by 1998 while discontinued import of DDT in 1983/84, stopped its local production in 1992 and prohibited allowing restricted its use following draft National Implementation Plan (NIP) preparation in 2005. Endrin received through grants was used in the irrigated HYV rice up to 1970, after which it was never imported and used in Bangladesh. Other POPs pesticides such as Toxaphene and Mirex were never imported and used in Bangladesh. Heptachlor, Chlordane, Dieldrin and Aldrin were used in controlling mostly soil pests like termites, white grub, cutworm and mole cricket in sugarcane, jute, vegetables and pulses, while DDT was used against mosquito for controlling malaria, and BHC was used in storage against stored grain pests. At present all these POPs pesticides have been substituted with mostly organophosphate, synthetic pyrethroid and carbamate insecticides but with very limited integrated pest management (IPM) practices comprising alternative to pesticides.

In preparing its National Implementation Plan (NIP) for the Stockholm Convention, the inventory of POPs pesticides prepared in February 2005 estimated a total of 495.69 MT of obsolete POPs pesticides of which DDT alone constitutes 482.90 MT. This amount of DDT in fact, is the remnants of 500 MT of DDT imported under ADB loan from Pakistan in 1983/84, which was not accepted due to substandard quality. That entire amount of DDT has been stockpiled in 4 stores at the Medical Sub Depot (MSD) in Chittagong since 1984. The stores have become too old, cracked in many places, doors have broken, floors have damaged, and thus the DDT has leached, spread over ground, dispersed in air, affected human health and polluted the whole environment. Considering the seriousness of the problem, Department of Environment (DOE), the focal point of Stockholm Convention in Bangladesh, requested FAO for its assistance to find a way out for its disposal. Thus a FAO mission financed by TCPF funds administered by FAOR Bangladesh studied the overall situation during 5 – 12 November, 2007 and proposed for a project preparation. The Mission identified a case pending in the court to settle the disputes of Government of Bangladesh vis-à-vis actual ownership of the DDT, which must be resolved before submitting any proposal for its disposal. Unfortunately the Government has yet not taken any effective initiative to resolve the issue. Thus the situation has further worsen and adverse effects of the DDT stockpiles are apprehended to multiply everyday causing serious damage to the human health near its vicinity, animal health in and around the city and polluting the environment as a whole. Besides, another 32.00 MT of Microcell/Wassalom raw materials needed for DDT production still exist in Bangladesh Chemical Industries Cooperation (BCIC) warehouse in Chittagong. In addition to POPs pesticides, 13.65 MT of obsoletes non-POPs pesticides are also lying in different godowns of the Department of Agricultural Extension (DAE).

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

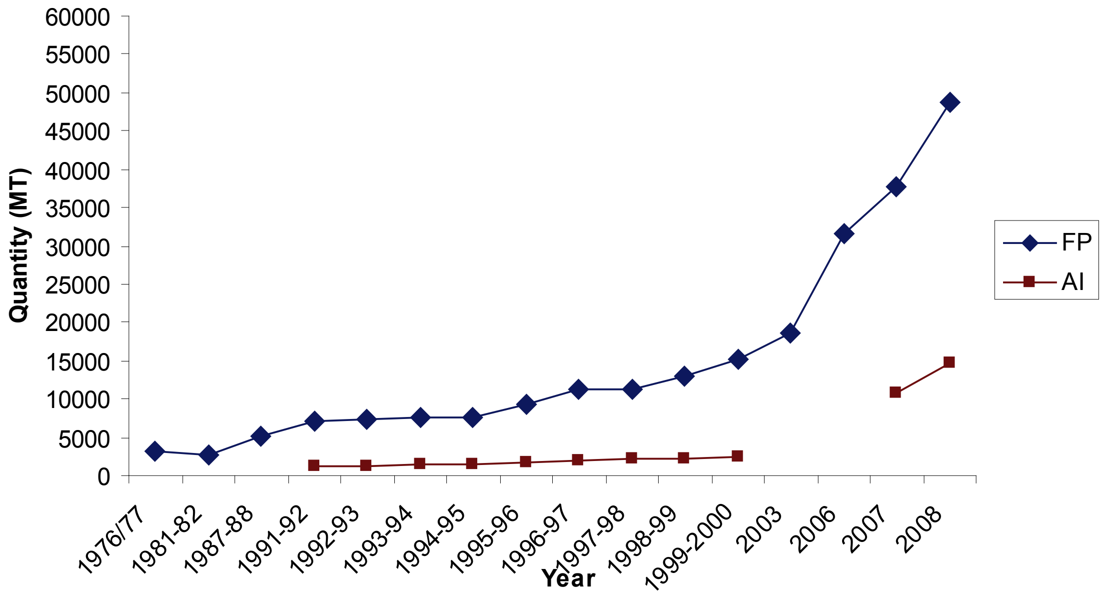
Introduction

Bangladesh, an agrarian country with an area of 1,47,570 sq. km, lies in the north eastern part of South Asia between 20°34' and 26°38' north latitude and $88^0$0l' and 92°41^I east longitude. It enjoys a subtropical monsoon climate. Temperatures range from a minimum of 7° - 13° Celsius (45°F - 55°F) to 24° - 31° Celsius (75°F - 85°F). The maximum temperature recorded in summer months is 37° Celsius (98°F), although in some places the temperature reaches 40° Celsius (105°F) 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 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 by 1998 except DDT for restricted use in case of emergency against mosquito, the vector of malaria. These actions have left a number of pesticides obsolete including the largest quantity of DDT stockpiles. Another important consequence of such banning and/or discontinuation the POPs and other hazardous pesticides has been the dominant use of other classes of pesticides like organophosphates, carbamates, synthetic pyrethroids due to absence of adequate effective alternatives for integrated pest management (IPM). This article has been prepared to make an account of such obsolete pesticides and the replacement status of POPs pesticides with alternatives. The article has been prepared based on the information available from various published articles, reports and recent observations.

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 l). The pesticide consumption in the country reached 15,160.00 MT of Formulated Product (FP) and 2,443.1 1 MT of Active Ingredient (AI) in 2000 as against only 3,134 MT of FP in 1977 (Rahman 2007), while it went up to 54,000 MT FP and 14,700 MT A.I. in 2008 (BCPA 2009). The registration of organochlorine pesticides had either been cancelled or withdrawn by 1997 (Rahman, 2004).

Figure 1. Trend of pesticides use in Bangladesh during 1976/77 to 2008 in Bangladesh



Pesticide Management Actions in Bangladesh and Status of POPs/Organochlorine pesticides

Bangladesh strictly follows the Pesticides Legislation developed in accordance with the FAO International Code of Conduct on the Distribution and Use of Pesticides, and thus in compliance with its legislation, WHO, Stockholm convention, Rotterdam Convention and Montreal Protocol it started discontinuing/banning/deregistering extremely hazardous pesticides in the 70's, and lastly banned Heptachlor in 1998.

The POPs pesticides, which have been discontinued, banned or deregistered include Endrin and BHC (1970), Aldrin (1975), Chlordane (1985), Dieldrin (1997), Heptachlor (1998) and imposed only restricted use permission for DDT (2005). The other POPs pesticides such as Toxaphene and Mirex were never imported and used.

Thus 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 including POPs pesticides. Among the obsolete pesticides, the DDT stockpiles are of serious concern.

DDT Issue

The use of DDT received through Grant/Barter was started against Malaria vector in 1965 followed by import. Bangladesh through establishing Chittagong Chemical Complex (CCC) at Barabkundu in Sitakundu, Chittagong started DDT production in 1966/67 and continued production up to 1991/92. The total production included Technical Grade 7706.49 MT, which were formulated into 12003.17 MT 75%WP, which was used up completely. It stopped production of DDT in 1993 and also stopped general use of DDT in 1992/93. Bangladesh signed Stockholm Convention in 2001, submitted draft NIP in 2005 and completely stopped use of DDT in 2005 allowing some highly restricted use during emergency against mosquito

vector to control malaria. Bangladesh became Party to the Stockholm Convention (COP) on 12.03. 2007.
Bangladesh completely stopped the import of DDT in 1984/85. Last deal of DDT import was in 1983/84 from Pakistan under ADB Loan. As per this deal, 500 MT of DDT was imported but due to sub-standard it was not received. This quantity was stored in 4 Medical Sub-Depots (MSDs) in Chittagong under the Ministry of Health. In a survey, a total of 482.904 MT were found in 18,2000 cartoons held in those four MSD warehouses, all in poor or obsolete condition (GoB/EADS 2005).

Actual Obsolete POPs Pesticides in Stock

The actual obsolete POPs pesticides in stock include: (i) imported DDT in MSDs: 482.904 MTs in 4 MSDs, (ii) DDT Technical 101.69 MT at BCIC, Chittagong, (iii) DDT 75 WP (local): 12.795 MT in District stores of Directorate of Health), (iv) DDT 75 WP (local): 0.005 MT at District stores of Department of Agricultural Extension (DAE), (v) Dieldrin 20EC: 1.350 MT in District & Thana stores of DAE. All these POPs pesticides sum-up to 603.739 MT. Besides a total of 13.668 MT non-POPs are stored in District DAE stores (GOB/EADS, 2005).

Government Strategy to Pest Control in Bangladesh

The Government is very much keen to reduce the sole reliance on pesticides in pest control and thus has been advocating the strategy as depicted in Figures 1 and 2. A number of alternative technologies are advocated as shown in Figure 2, which are not so effective, and thus their adoption by farmers is very poor. The reality is that due to absence of appropriate alternatives, the strategy is yet to be effective as may be seen in Table 1. The table indicates that the POPs pesticides have been substituted by pesticides belonging to mostly organophopsphates, carbamates and synthetic pyrethroids, and not by the alternative technologies, and thus the dominance or sole reliance on pesticides still persist in the country. This is also evident from the increased import and consumption of pesticides as shown in Figure 1.

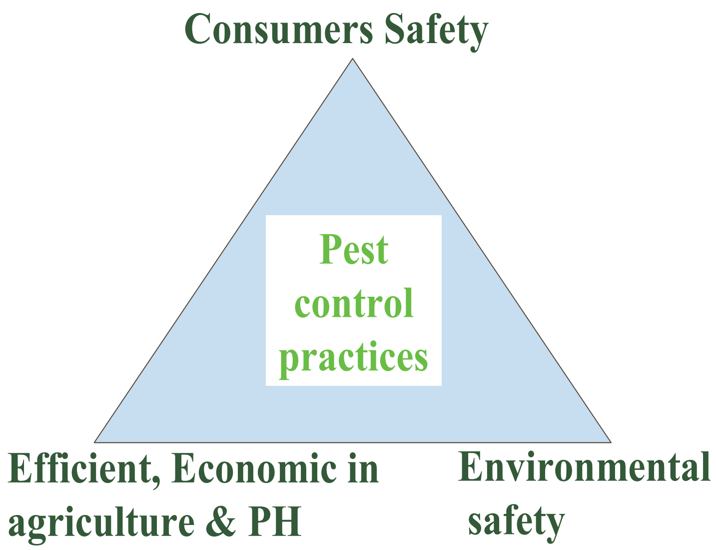


Table 1. Substitutes of POPs pesticides for managing pests in Bangladesh

Crops/Public Health	**Pests**	**Replaced POPs Pesticides**	**POPs Substitute Pesticides**	**Effective and widely adopted Alternative to pesticides**
Potato	Cutworm	Dieldrin, Heptachlor	Bifenthrin, Carbofuran, Cartap, Chlorpyrifos, Chlorpyrifos methyl, Lambda Cyhalothrin, Diazinon	None
Sugarcane	White Grub & termite	Heptachlor Dieldrin	Bifenthrin, Cadusafos	None
	Termite	Heptachlor, Dieldrin	Carbofuran, Chlorpyrifos, Chlorpyrifos + Alpha-Cypermethrin, Permethrin, Imidacloprid, Thiamethoxam	None
Tea	Termite	Chlordane Dieldrin	Bifenthrin, Chlorpyrifos, Permethrin, Imidacloprid, Thiamethoxam	None
Jute	Mole Cricket	Heptachlor, Chlordane, Dieldrin		None
Maize	Cutworm		Chlorpyrifos, Lambda Cyhalothrin	None
Rice	Stored Grain insects		Fenitrothion, Pirimiphos methyl, Aluminium Phosphide	None
Vegetables	Cutworm	Chlordane		None
-	Soil insects	Chlordane, Dieldrin		None
Public Health	Mosquito	DDT	Cypermethrin, Malathion, Malathion + Permethrin, Lambda Cyhalothrin, d-allethrin, Permethrin, Tetramethrin, Temephos, Phenthoate, Alpha Cypermethrin, Deltamethrin, S. Bioallethrin + Permethrin, d-transallethrin, Allethrin, Esbiothrin, S. Bioallethrin + permethrin + PBO, ETOC (Prallethrin), ETOC & Sumithrin (d-Pheothrin)	Bed nets Impregnated bed net Coils, Aerosols (Limited use)

POPs Pesticides Disposal Status

The obsolete pesticides comprising mostly DDT are still a serious concern, which could not be disposed of but are lying in different places with around 500 MTs in two places in a district (Chittagong), which are causing serious health hazards and environmental contamination due to their dispersion, leaching and misuse. Department of Environment (DOE), the focal point of Stockholm Convention in Bangladesh, requested FAO for its assistance to find a way out for its disposal. Thus a FAO mission with Mr. Mark Davis as the Mission Leader financed by TCPF funds administered by FAOR Bangladesh studied the overall situation during 5 – 12 November, 2007 and proposed for a project preparation. The Mission identified a case pending in the court to settle the disputes of Government of Bangladesh vis-à-vis actual ownership of the DDT, which must be resolved before submitting any proposal for its disposal. The mission made the preliminary assessment and drafted project proposal. But due to lack of co-financing the initiative taken by FAO is uncertain.

Conclusion and Recommendations

The obsolete pesticides are causing serious adverse effects to the human health and environment as a whole. The POPs pesticides have been substituted mostly by other classes of pesticides. The effective alternatives to the pesticides including POPs pesticides are rare.
Under the above context, effective cooperation from the international community for disposing of all wastes/obsolete pesticides already identified in stocks is essential. Along with this, the concerned international community should consider very seriously for comprehensive interventions and programmes for developing effective alternatives to the POPs pesticides. Otherwise, the POPs pesticides will be substituted by other classes of pesticides, which in the future, may appear as a new threat to the human health and the environment as a whole.

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INVENTORY OF OBSOLETE PESTICIDE STORAGE SITES TO MINIMIZE ECOLOGICAL RISK IN KAZAKHSTAN

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Abstract

In Kazakhstan, a deepening ecological crisis has been caused by contamination of the environment with obsolete and expired pesticides. Large-scale physical and chemical technologies for managing pesticidecontaminated soils are expensive and unacceptable for Kazakhstan because of limited financial resources. Phytoremediation is a promising innovative technology for managing pesticide-contaminated soils. Pesticide contamination is common on land surrounding destroyed warehouses that were part of the official plant protection service of the former Soviet Union. We surveyed substances stored in 76 former pesticide warehouses in Almaty and Akmola oblasts of Kazakhstan to demonstrate an inventory process needed to understand the obsolete pesticide problem throughout the country. The survey areas were within 250 km of Almaty (the former capitol of Kazakhstan) and within 100 km of Astana (the new capitol). In Almaty oblast, a total of 352.6 tonnes of obsolete pesticides and 250 pesticide containers were observed. In Akmola oblast, 36.0 tonnes of obsolete pesticides and 263 pesticide containers were observed. Persistent organic pollutants (POPs) pesticides contaminated soil around 26 of the former storehouses where the concentration of POPs exceed the Kazakhstan MAC (maximum allowable concentration) for soil contaminated by 10 to hundreds of times. The POPs pesticides include metabolites of DDT (dichlorodiphenyltrichloroethane) and isomers of HCH (hexachlorocyclohexane).

Keywords: obsolete pesticides, phytoremediation, DDT, HCH, pesticide tolerance, inventory

1. Introduction

Kazakhstan became independent from the former Soviet Union in 1991; however, many of the impending environmental problems were not anticipated. Within five years of independence, pesticide storage warehouses that used to be managed by the official plant protection service of the former Soviet Union were destroyed, leaving obsolete pesticides and their containers unattended and open to the environment. Most of the bulk obsolete pesticides have been moved to other storage areas, taken by citizens for individual use, resold, or released into the surrounding environment with no indication of their potential danger to local residents. Much of the obsolete pesticides that were resold were first repackaged in unlabeled or mislabeled containers. People living around the warehouse sites often use the land for pasture, kitchen gardens, and play areas for children, and as a source of construction materials.

Pollution of soil and water by obsolete pesticides is a serious ecological problem. Many of these former warehouses have become hot points of contamination and represent a serious ecological danger.

The Republic of Kazakhstan government has developed laws to address this situation; however, it is necessary to implement these laws. Official data on the number of warehouses, their location, the fate of bulk pesticides, and quantities of buried or unburied pesticides are inconsistent for different regions and for Kazakhstan as a whole. For example, the Ministry for Environmental Protection estimates the Almaty area has burial places with more than 87 tons of pesticides, while the Ministry of Agriculture estimates this area has about 126 tons of buried pesticides. Bismildin (1997) stated that Kazakhstan accumulated 574 tons of obsolete pesticides, while Nazhmetdinova (2001) estimated accumulation of one million tons of pesticides.

Kazakhstan signed the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2001 and ratified the treaty in 2007. In 2004, a Global Environment Facility sponsored project to provide initial support for the performance of Kazakhstan’s obligations under the Stockholm Convention estimated there were 1500 tons of obsolete pesticides and pesticide mixtures. The project suggested that many of the mixtures contained POPs pesticides (UNEP, 2004). This initial inventory of obsolete pesticides described only the condition of pesticide storehouses and quantities and conditions of pesticide containers. There has been insufficient scientific study to estimate the danger to public health and the environment from these sites. Mass media within Kazakhstan has not given sufficient attention to the problem of chemical contamination of the environment. Many different methods can be used for remediation of pesticides in soil. Some large-scale and expensive remediation technologies that may be effective for treatment of pesticide-contaminated soil and water are likely to be unacceptable in Kazakhstan due to limited financial resources.

Phytotechnologies use vegetation to accumulate, degrade, or stabilize environmental contaminants. Innovative natural remediation technologies like phytoremediation are promising if they can be shown to address cleanup requirements and can be effectively managed at an acceptable cost.

The strategy for this project was to identify pesticide-tolerant plant genotypes which can be used for phytoremediation of pesticide contaminated soil in the Almaty and Akmola oblasts of Kazakhstan.

In this study, pesticide analysis was limited to the organochlorine pesticides DDT (p,p'-dichlorodiphenyltrichloroethane) and HCH (hexachlorocyclohexane), along with their associated metabolites and isomers: 2,4 DDD (p,p'-dichlorodiphenyl dichloroethane); 4,4 DDD; 4,4 DDT; 4,4 DDE (p,p'-dichlorodiphenyldichloroethylene); α-HCH; β-HCH; and γ-HCH). While these pesticides represent only a subset of all obsolete pesticides, they are important due to their status as persistent organic pollutants and as compounds that represent a much larger problem.

2. Methods and results

2.1. TASK 1: INVENTORY FORMER OBSOLETE PESTICIDE WAREHOUSES TO DOCUMENT OBSOLETE PESTICIDE STOCKPILES AND TO CHARACTERIZE LEVELS OF SOIL CONTAMINATION

To address problems associated with obsolete pesticides in Kazakhstan, it is critical to understand the scope of the problem and the location of affected areas. Since Kazakhstan is a very large country, we chose to initially survey two regions to demonstrate an inventory process that could be applied more widely when sufficient resources are available. The largest warehouses of the Soviet plant protection service in Kazakhstan were located in Almaty and Akmola oblasts because of the administrative importance and level of agricultural development in these regions. We surveyed obsolete pesticide storehouses in 10 of 14 rayons or districts in Almaty oblast and five rayons of Akmola oblast. In each rayon, the Ministry of Agriculture Department of Plant Protection was contacted to obtain locations of former pesticide storehouses and permission to access the sites. Local government authorities were contacted to receive further information on locations and permission to survey and sample each site.

In this paper, we refer to the former storehouse sites where we have observed pesticide contamination as "hot points." Based on the history of agriculture in these areas, we assumed the hot points were chemically heterogeneous, and probably contained not only organochlorine pesticides, but also other classes of pesticides and fertilizers. Our study focused on analysis of organochlorine pesticides as markers of field contamination due to their status as persistent organic pollutants and their prevalence. We took more than 800 soil samples to determine residual pesticide concentrations using standard methods adopted by the United States Environmental Protection Agency. All soil samples were extracted using the solvent dichloromethane that was boiled and cycled for several house using a Soxhlet apparatus. Soil extracts were analyzed using an HP6890 gas chromatograph equipped with an electron capture detector and a capillary column using EPA method 8081 (USEPA, 2007).

A total of 76 former storehouses were surveyed in Almaty and Akmola oblasts. All storehouse buildings were either partially or completely destroyed. The inventory included descriptions of conditions of the storehouse structures; estimation of bulk obsolete pesticide stockpiles and pesticide containers, inspection of storehouses and surrounding areas for pesticide contamination, assessment of vegetation growing at the sites, and public outreach. An inventory worksheet was developed to provide a systematic description of each location.

In Almaty oblast, a total of 352.6 tonnes of obsolete pesticides and unidentified stockpile material were observed. We also observed 250 pesticide containers. In Akmola oblast, a total of 36.0 tonnes of obsolete pesticides and unidentified stockpile material were observed, along with 263 pesticide containers (Table 1).

In Almaty oblast, several different classes of substances were identified. Much of the bulk chemical substances did not have readable labels and remain unidentified. The following classes of pesticides were observed: triazine herbicides (atrazine, protrazine, propazine, simazine) organophosphate insecticides (metaphos or methyl parathione), organochlorines (nitrophen and illoxan or diclofop-methyl), dinitroanaline herbicides (treflan), carbamate (temik or aldicarb), and a pesticide mixture including compounds labeled Thiram and Hataonyag.

Total amount of identified obsolete pesticides was 36,620 kg. The amount of identified pesticides that are forbidden or banned was 350 kg. In Almaty oblast, the quantity of unidentified mixtures of obsolete pesticides was 315,980 kg or 89.6% of the total obsolete pesticide stockpiles.

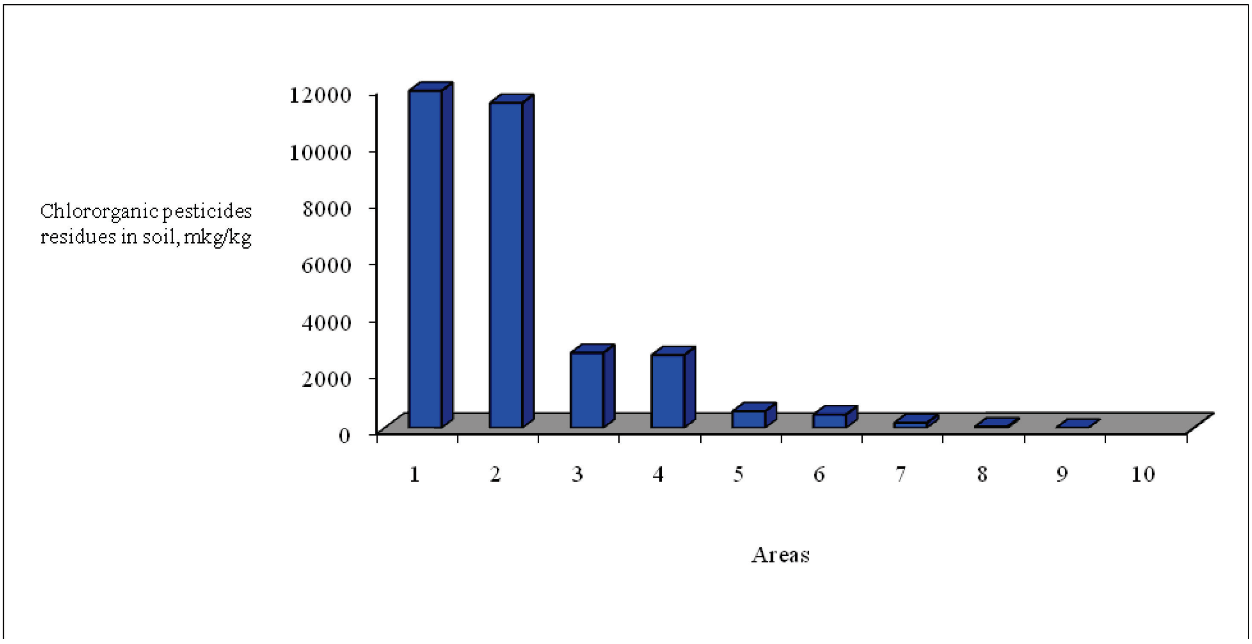
In Akmola oblast, 100% of the 36,045 kg of obsolete pesticide stockpiles was unidentified chemical mixtures.

Table 1. Quantities of obsolete, forbidden, and unidentified pesticides in former warehouses in Almaty and Akmola oblasts of the Republic of Kazakhstan.

Areas	Identified obsolete pesticides (kg)	Banned pesticides (kg)	Unidentified substances (kg)
Almaty oblast			
Karasajsk			1150
Talgar	30600		
Dzhambul	200		100500
Enbekzhi-Kazakh	2950	350	4570
Uigur	970		2860
Balkazh			500
Ulisk	1450		105700
Eskeldinsk	50		100700
Kerbulak	0		
Koksuisk	0		
Total	**36620**	**350**	**315980**
Akmola oblast			
Atbasar	3		26430
Buladinsk	2		5345
Enbekshilder	2		900
Zharkain	1		700
Shortandi	4		2670
Total	12		**36045**

Soil samples were collected from each pesticide storehouse site to examine migration and expansion of pollution. Sites where soil contamination was observed in excess of maximum acceptable concentrations (MAC) for the Republic of Kazakhstan (1996, 2001, 2003) were called hot points. Twenty-six of the storehouse sites showed soil concentrations in excess of MACs. The MAC for Kazakhstan for soil is 100 µg/kg for the DDT metabolites (4,4 DDT; 4,4 DDE) and HCH isomers (β-HCH; γ-HCH). Three compounds we analyzed did not have MAC for Kazakhstan 2,4 DDD, 4,4 DDD, and α-HCH.

The most polluted storehouses were four sites located in Almaty oblast in the rayons of Eskeldinsk, Talgar, Karasajsk, and Enbekzhi-Kazakh where concentrations of organochlorine pesticides exceeded MAC up to 114 times (Figure 1).



1– Eskildinsk area, 2 –Talgar area, 3 –Karasajsk area, 4 – Enbekzhi-Kazakh area, 5 – Dzhambul area, 6 – Balhash area, 7 – Ilijsk area, 8 – Uigur area, 9 –Kerbulaksk area

Figure 1. Total soil concentrations of isomers of HCH and metabolites of DDT from former pesticide storehouses in Almaty oblast.

The most common pollutants were α-HCH, β-HCH, 4,4 DDE, and 4,4 DDT. For example, in the village of Aldabergenova in Eskedinsk rayon, concentrations of 4,4 DDT exceeded MAC by 19 times (1955 ± 69 μg/kg), 4,4 DDE by 28 times (2867 ± 68 μg/kg), and β-HCH by 17 times (1731 ± 117 μg/kg). In the village of Kyzyl-Gairar in Talgar rayon, α-HCH was observed to be 1239 ± 136 μg/kg; 2,4 DDD; 398 ± 8 μg/kg; and 4,4 DDD, 1899 ± 42μg/kg. In Balkhazh, Uigur and Ilijsk rayons, insignificant amounts of HCH isomers were observed. Although α-HCH has no MAC, since isomers of HCH are known to be highly toxic and mutagenic (Medved, 1977), there is cause for concern about soil contaminated with this compound.

Residual metabolites of DDT and HCH isomers we observed in soil do not depend on the presence or absence of bulk, obsolete pesticide stockpiles at the storehouses. For example, in the village of Belbulak in Karasajsk rayon, 500 kg of unidentified white powders were observed open to the air.

Observed soil concentrations of 4,4 DDT exceeded MAC by 16 times (1670± 66 μg/kg) and 4,4 DDE exceeded MAC by eight times (852 ± 18 μg/kg). In the village of Kyzyl-Gairar in Talgar rayon, no pesticide stockpiles were observed but soil concentrations of 4,4 DDT exceeded MAC by 65 times (6584 ± 207 μg/kg) and 4,4 DDE by 20 times (2097 ± 54 μg/kg).

Control soil batches were sampled at least 800 meters from each hot point in Karasajsk rayon. The control samples contained α-HCH and some metabolites of DDT, primarily 4,4 DDE and 4,4 DDT, but these did not exceed MAC.

In Almaty oblast, several lakes are located near former storehouses in Talgar and Dzhambul rayons. Lake water was sampled from one lake in each of these areas. Two water samples from a lake located 100 m from a storehouse in the village of Beskanar in Talgar rayon contained an average of 114 μg/L 4,4 DDE. Maximum concentration of pesticides observed in soil around the storehouse in this area was 1660 μg/kg. Chemical exposure to humans could result from contact or consumption of water, or fish from the lake.

These data demonstrate the potential ecological danger and health risk posed by the former pesticide storehouses, especially those located near populated areas. Resolution of this risk will require elimination of obsolete pesticide stockpiles and pesticide containers, including locations where pesticides have been buried. Further priorities include remediation of soil polluted by organochlorine pesticides. Screening pesticide polluted sites will provide a basis for development of an action plan to prevent or minimize ecological risk from pesticide pollution in Kazakhstan. Results of inventories and inspection of former pesticide storehouses provide an additional source of data for official inventory of obsolete pesticide stocks, and for development and conduct of public and state programs and projects on preservation of the environment and maintenance of ecological safety.

To analyze genotoxicity of organochlorine pesticides, we analyzed chromosome structural mutations observed during the metaphase stage of mitosis in meristem cells of barley seed. Seeds of *Hordeum vulgare* L. variety Odessa-100 were treated using pesticide concentrations observed in soil around former storehouses. To treat barley seed with pesticides, air dried seeds were immersed for four hours in hexane solutions used to dissolve HCH isomers and DDT metabolites. Two control treatments included seeds wetted with only distilled water and seeds wetted with only hexane. Seeds were washed, slightly dried, and germinated on filter paper moistened with distilled water at 25 ± 1°C. Prior to fixation of cells for staining, seeds were transferred to a solution of 0.01% colchicine. Fixation of chromosomes was accomplished by placing macerated roots in a solution of 0.002 M 8-oxyquinoline for one hour at 13-15°C. Cytogenetic preparations were made using standard techniques (Paucheva, 1974). More than 300 metaphase cells were examined for each treatment. Analysis of chromosomal reorganizations for different fixings did not show significant differences; therefore, analysis of results was based on all data. Analysis of chromosome structural mutations took into account not only the total of all abnormalities, but also types of chromosomal and chromatid aberrations including isolocus chromosome breaks and micro fragments

Control observations recorded spontaneous mutations in seed that was not exposed to pesticides. Results of cytogenetic analysis showed that not all tested concentrations of HCH isomers and DDT metabolites resulted in chromosome aberrations significantly exceeding control treatments (Table 2). Frequency of chromosome aberrations for the water control was 2.9 ± 0.9% and 3.4 ± 0.2% for the hexane control. Aberrations observed in the water control were limited to terminal deletions (1.4 ± 0.4%) and isolocus breaks (1.5 ± 0.5%). Aberrations for the hexane control were microfragments (1.2 ± 0.3 %), isolocus breaks (1.7 ± 0.2 %), and single fragments (0.5 ± 0.1 %).

Significant excess chromosomal mutations were observed in treatments by HCH isomers. Aberrations from γ-HCH treatments were 13.9 ± 1.9% for concentrations of the MAC and 15.6 ± 2.0% for concentrations of two times the MAC. For β-HCH, the treatment of eight times the MAC resulted in excess aberrations of 11.7 ± 1.7%. For α-HCH, aberration frequency was 8.5 ± 1.6% for the treatment concentration of 50 μg/kg and 15.5 ± 2.0% for the treatment concentration of 200 μg/kg. The main types of aberrant chromosomes for pesticide treated barley seed were centric and acentric rings, as well as dicentric and isolocus breaks.

For treatments with DDT metabolites, excess aberrations were observed for several treatments: 4,4 DDT in concentrations of five MAC (16.0 ±2.0%); 2,4 DDD in concentrations of 50 μg/kg (12.2 ± 1.8%) and in concentrations of 100 μg/kg (13.07 ± 1.9%); 4,4 DDE at the MAC (12.5 ±1.7%); and 18 times the MAC (14.3 ± 1.9%). DDT metabolites induced all types of chromosomal aberrations including centric and acentric rings, dicentric rings, single fragments, micro fragments, isolocus breaks, and asymmetric chromatid translocations.

Observations of chromosomal mutations from pesticide-treated barley seed using concentrations similar to those found in the soil at hot points suggest health risk from potential exposure to contaminated soil around former warehouses.

To investigate potential use of phytoremediation, we delineated the following seven tasks:

Task 1: Inventory former obsolete pesticide warehouses to document obsolete pesticide stockpiles and to characterize levels of soil contamination.

Task 2: Study genotoxicity of organochlorine pesticides.

Task 3: Identify pesticide-tolerant plant species using surveys of plant community structure at selected “hot points”.

Task 4: Describe physiological and biochemical characteristics of pesticide-tolerant plants grown in pesticide-contaminated soil.

Task 5: Document pesticide accumulation patterns in pesticide-tolerant plants.

Task 6: Study the fate and transport of pesticides in soil and plants in the greenhouse using soil collected from hot points.

Task 7: Study the effect of fertilization on phytoremediation potential in the greenhouse and field.

We studied plant community structure at six “hot points” contaminated sites with three located in Almaty oblast and three in Akmola oblast. From these studies, 17 pesticide-tolerant plant species were selected from colonizing plants that grew near the centers of the hot points. A greenhouse experiment using the pesticide-tolerant species showed some plant species have the ability to change plant growth characteristics when grown in contaminated versus uncontaminated soil. These characteristics include biomass production, rate of phonological development, peroxidase activity in roots and leaves, ratio of chlorophyll a to chlorophyll b, rate of evapotranspiration, and phytoaccumulation of organochlorine pesticides and their metabolites (4,4 DDE, 2,4 DDD, 4,4 DDT, α-HCH, β-HCH and γ-HCH). We observed pesticide accumulation was influenced by plant species, plant biomass, and soil pesticide concentrations. Among the investigated species, four accumulated metabolites of DDT and isomers of HCH in plant tissue concentrations exceeding the Kazakhstan MAC (maximum acceptable concentration) for plant tissue by 400 times. The Kazakhstan MAC for DDT and HCH metabolites in plant tissue is 20 μg/kg. Species in this category included: *Artemisia annua* L., *Kochia sieversiana* (Pall.) C.A. Mey. *Kochia scoparia* (L.) Schrad., and *Xanthium strumarium* L. Three species exceeded the MAC by up to 90 times including *A. annua, Ambrosia artemisiifolia* L., and *Erigeron canadensis* L. Most pesticides accumulated in the root systems; however, among the species investigated, *K.scoparia, A. annua, Barbarea vulgaris* W. T. Aiton, and *A. artemisiifolia*
demonstrated capabilities to translocate pesticides from roots to aboveground tissues. To help identify the location of accumulated pesticides within plant tissue, we employed histological analysis whereby a few species indicated pesticides were distributed unevenly within different plant tissues. If a species had a dorsiventral and isolateral leaf type, then pesticides appeared to accumulate in palisade mesophyll tissue. If a species had homogeneous mesophyll, then pesticide appeared to accumulate in mesophyllous cells around conducting bunches. For example, *X. strumarium*. has a dorsiventral type of leaf; thus, pesticides collected in the palisade mesophyll. In the stem, pesticides accumulated in walls of xylem cells. In root tissue, pesticides accumulated in parenchymous cells and xylem walls. We investigated cultivation methods to enhance plant uptake of pesticides. Use of mineral fertilizers resulted in stimulation of growth and biomass accumulation that increased phytoextraction. The concentration of DDT metabolites and isomers of HCH in soil and the application of

fertilizers lengthened the rate of phenological development increasing plant height and biomass. In a greenhouse experiment using fertilizer applications to pesticide-contaminated soil, tolerant species showed increased phytoextraction of pesticides. Phytoextraction by *X. strumarium* increased

from 0.3% to 0.6 %, *A. annua* from 0.5% to 0.7 %, and *Cucurbita pepo* L. *pepo* from 0.4 to 0.7 %. *K. scoparia and Amaranthus retroflexus* L. showed high bioaccumulations factors but showed low biomass compared to other species and thus weak phytoextraction. *A.annua, K. scoparia, A. retroflexus*, and *X. strumarium* decreased pesticide concentration of rhizosphere soil 11-24 % more in treatments with fertilizer compared to treatments without fertilizer.

Field experiments using selected wild species demonstrated reduction of pesticide concentrations in soil in excess of reductions observed without plants and without fertilizers.

Additional work is needed to determine if practically useful phytotechnology applications can effectively manage pesticide-contaminated soil at former storehouse sites.

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NATIONAL IMPLEMENTATION PLAN FOR STOCKHOLM CONVENTION – ACTION PLAN FOR POPs AND OBSOLETE PESTICIDES – case study – REPUBLIC OF SERBIA

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Abstract
With the financial aid provided by the Global Environmental Facility (GEF) of the United Nations and in cooperation with the United Nations Environmental Program (UNEP), the Ministry of Environment and Spatial Planning of the Republic of Serbia has developed the National Implementation Plan (NIP) for the Stockholm Convention within the scope of the project "Enabling Activities for the Development of a National Plan for Implementation of the Stockholm Convention on Persistent Organic Pollutants- POPs",
One of the components of POPs inventory represents the inventory of organochlorine pesticides POPs pesticides, as well as inventory compilation of all waste pesticides in territory of the Republic of Serbia
This paper deals with current state of POPs and obsolete pesticides management in Serbia. In the paper are also presented results of the National Plan for Implementation of the Stockholm Convention on Persistent Organic Pollutants- addressing particularly on POPs pesticides

Introduction
POPs project has been carried out in five phases:
- determination of project coordination and organization mechanisms;
- compilation of POPs preliminary inventory and infrastructure and capacity estimate;
- setting priorities and goals;
- development of draft NIP, as well as preparation of specific action plans;
- finalization of the NIP and its approval by all interested parties.

The main outcome of the POPs project is development of the NIP. NIP was prepared as a realistic and comprehensive document, providing a solid base for determining further activities on implementation of the provisions of the Stockholm Convention.
In addition, the project was methodologically carried out in a manner which had ensured involvement of large number of interested parties and competent organizational units within the ministry responsible for environmental protection. The most valuable feature of the project is appropriate involvement of key individuals and institutions, ensuring allocation of planned activities and introduction of issues of pops management into new regulations, education plans and other plans necessary for fulfillment of obligations under the Stockholm Convention

NIP is comprised of two parts:
1. The first part provides general information on the Republic of Serbia, information on Serbian legislation in the fields of environmental protection and chemicals, with special consideration given to POPs and their estimated quantities based on the preliminary inventory compiled.
2. The second part of the Plan contains a strategy for Convention implementation, as well as appropriate action plans : Action plan for dealing with the obsolete pesticides

(pesticide waste); Action plan for dealing with PCBs; Action plan for dealing with uPOPs (PCDDs/PCDFs, PCBs and HCB); Action plan considering institutional and regulatory measures aimed at Stockholm Convention implementation and reporting; Action plan considering monitoring; Action plan for contaminated areas and development; Strategy for public informing, awareness raising and education and action plan for strategy implementation

Pesticide production

Production of pesticides in the previous century in Serbia has to be considered within the scope of pesticide production in Socialist Federal Republic of Yugoslavia (hereinafter former Yugoslavia). Until the early eighties of the last century, the industry of former Yugoslavia had synthesized 18 pesticides.

Today, pesticides are produced in about twenty Serbian companies, including several private entrepreneurs offering exclusively formulated products. Total domestic production of plant protection and nourishment products is estimated to approximately 60,000 t/a (excluding capacities producing copper-sulphates and other copper compound based plant protection products).

Production of POPs pesticides in Serbia, started in 1947, in the beginning included only production of DDT in "Zorka - Zaštita bilja" in Šabac. Other compounds (aldrin, dieldrin, endrin, toxaphene, chlordane, heptachlor and hexachlorobenzene) were imported as technical preparations to be used for production of plant protection products in factories "Zorka - Zaštita bilja" in Šabac, "Župa" in Kruševac and "Galenika" in Zemun. The production of plant protection products was discontinued in accordance with decisions on prohibited use and trade of preparations based on the above specified active substances.

It should be stressed out that pesticides listed in the Stockholm Convention were prohibited from agricultural trading and use in Serbia during the seventies and the eighties of the last century. Use of DDT in the sector of public health had ceased in the early nineties of the last century.

Inventory of pesticides

POPs pesticides have been used in Serbia for many years in the fields of agriculture, animal and public health control and other activities. Their use was prohibited during the eighties of the last century. Today, POPs pesticides are not produced, imported or exported from Serbia.

The main problem in development inventory of pesticides was missing of proper data. As in other countries with economies in transition, in the Republic of Serbia there were no data or assembled data bases which could have been used for inventory assembling. In addition, economic entities were not legally obliged to submit the related data. In that way the preliminary inventories have been compiled based on the distributed questionnaires analysed by project consultants. Apart from project consultants, preliminary inventories of pesticides and uPOPs have been assembled with the help of inspection bodies. Such approach has helped not only to compile preliminary inventories, but to define methodology for detail inventory assembling.

Methodology for POPs and obsolete Inventory consisted of the following activities grouped in three phases:

1. Preparation phase included the following activities: Literature review, Critical analysis of available reports, Identification of key institutions and individuals to be involved in the report development, Preliminary visits and interviews, Development of methodology for POPs pesticide inventory compilation, Questionnaire development, Investigation plan preparation.

The following key target user groups have been identified: pesticide producers, pesticide users, pesticide importers and distributors, scientific institutes.

This phase of project realization has indicated that data collection through questionnaires distributed to the identified target user groups did not provide expected results and it was decided to engage the following inspection bureaux of the relevant ministries on the project activities: Environmental Protection Inspection Department and Phytosanitary Inspection Department.

2. Implementation phase – data collection

The following activities were carried out during the implementation phase: two inspector training sessions (for and questionnaire distribution,) data collection plan development and identification of target groups to be subject to examination. On the base of distributed questionnaires, data were collected through inspection of field investigations, via e-mail and by phone as well.

3. Realization phase and inventory compilation

During the realization phase, data obtained from the following sources have been analysed: Primary sources (from the user-filled questionnaires). Data collection from secondary sources, Data collection from field investigations and on-site inspections, Data verification for each individual location, Case studies.

In addition to previously specified preliminary inventories, are also collected information on current POPs stockpiles, contaminated areas and waste, data on remediation of contaminated areas, POPs levels in different environmental media, prediction of future POPs production, use and release, POPs monitoring in the Republic of Serbia, as well as current information, knowledge and education levels of each target group, mechanism for exchange of information with other signatories to the Convention.

Inventory

Preliminary inventory of waste pesticides has been compiled in the period May-September 2007. During the specified period, the following data had been collected:

- data on POPs pesticides;
- data on other pesticides including obsolete, out-of-date, unknown pesticides (pesticide waste); and
- pesticide packaging.

Obsolete pesticides are those containing active substances which are no longer produced due to variety of reasons (effectiveness, toxicological and eco-toxicological danger).

Out-of-date pesticides include preparations with expired use-by date, prohibited pesticides, damaged and degraded products, unusable preparations and packaging, unidentified products, empty contaminated packaging and old equipment used for pesticide application, other contaminated materials and containers, buried pesticides and containers, contaminated areas – soil (visual inspection).

During data collecting for the purpose of the preparation of preliminary inventory, 167.380 kg (app. 167 tonnes) of estimated mass of pesticide waste and 42.935 kg (app. 43 tonnes)of estimated mass of unidentified pesticides have been recorded. In addition, 128 pesticide waste storage facilities have been identified

Table 1. Inventory of pesticide waste

QUANTITY OF PESTICIDE BASED ON ITS STATE OF AGGREGATION	**solid** (kg)	**liquid** (l)	**estimated quantity (kg)**
POPs pesticides	2.310	3.940	***6.250***
Obsolete pesticides	122.371	45.009	***167.380***
Unidentified pesticides	36.415	6.520	***42.935***
Total	***161.096***	***55.469***	***216.565***
Packaging material			***112.076***

POPs pesticides have been detected in 14 locations,.

Table2. Quantities of detected POPs pesticides

QUANTITY OF POPs PESTICIDE	**solid (kg)**	**liquid (l)**	**estimated quantity(kg)**	**number of storage units**
DDT	250	200	450	2
Lindane	2.060	3.740	5.800	12
TOTAL	**2.310**	**3.940**	**6.250**	**14**

Conclusions on NIP

During NIP preparation there are several identified priorities such as:

- Complete establishment of relevant legislations and strengthening of stakeholders capacities for rising of public awareness regarding all POPs;
- Preparation of overview of import, production and use of new POPs;
- Sound waste management for proper handling of POPs waste and in order to avoid u POPs;
- Implementation of BAT/ BEP for avoidance of emission of u POPs in relevant industrial and other sectors;
- Identification and remediation of POPs contaminated sites on the environmentally sound manner;
- Addressing the obsolete pesticide issue and prevention of generation of new waste.

Main goal is:

Removal of POPs pesticides and pesticide waste, prevention of their future releases into the environment and inadequate management

Specific goals of Action plan for obsolete pesticides are:

1. **System for identification and sound pesticides packaging waste and pesticides waste management for existing pesticides waste quantities and empty pesticides containers established,**
2. **System for identification and sound pesticides packaging waste and pesticides waste management for future pesticides waste quantities and new empty pesticides containers established.**

1. System for identification and sound pesticides packaging waste and pesticides waste management for existing pesticides waste quantities and empty pesticides containers established	
Action	Description
Action 1.1: Establishment and management of Pesticides Coordination Committee.	Committee has following tasks for all pesticides related issues such as: Cooperation between stakeholders; Fast communication and solutions of administrative and technical problems; Back-up and guidance of inventory project and demonstration project for Management POPs pesticides waste and stocks at previous POPs Production Facility; To secure process of permit issuance, allowing collection, transport and storage of detected and future quantities of pesticides waste during all phases of the project (see Action 1.4.); Tackles other bottle necks. In order to provide the best manner of waste pesticide and packaging inventorying and collecting, it is necessary for all relevant ministries and bodies of municipal self-government to reach a consensus and confirm it by signing a Memorandum of Cooperation. This specially refers to the ministry responsible for agriculture (dealing with the issues of pesticide management and water management permit issuing), ministry responsible for environmental protection (waste management, environmental protection assessment, permit for planning, permit for construction work and use-permit issuance and chemical management) and municipal self-government (with respect to the location of planned adaptation or container installation).
Action 1.2: Define a manner for conducting Obsolete Pesticides and POPs waste management and conditions and procedures for obtaining permits allowing temporary hazardous waste storage, disposal and treatment..	Law on Waste Management defines hazardous waste and among them POPs waste management and authorizes development of sub-legal regulations which would import the provisions of Regulation (EC) 850/2004 into national legislation. The sublaw on POPs waste management shall define proper POPs pesticide handling. In order to fully regulate the issue of hazardous waste management, including POPs waste management, it is necessary to develop a set of sub-legal regulations related to procedures for obtaining permits allowing storage, disposal and treatment of hazardous waste, hazardous waste catalogue etc. Among the legislation development dealing with hazardous waste it is necessary to develop related gap analyses of existing system for obsolete waste management as well as plan for future activities.
Action 1.3: Capacity building for authorities, inspection, industry and other stakeholders for sound pesticides waste management.	Capacity building have to be established through training for trainers for following issues: 1. Inventory for pesticides waste (securing that all trainers for each district have been trained and can execute own training in their district). This training should include training for data collecting, based on experiences in preliminary inventory and FAO Standard Approach for inventory using FAO PSMS (Pesticides Stockpile Management System) with Server based data management system; 2. Risk assessment system and prioritization and selection of temporary storage and collection centers for pesticides waste (using FAO PSMS); 3. Professionals for repacking of obsolete pesticides, possible destruction technologies for pesticides and packaging waste; 4. Necessary requirements for permits issuing for temporary storage and necessary management system for assuring appropriate storage of pesticides waste.
Action 1.4: Pilot demonstration inventory project for one selected district, for POPs and other waste pesticides and propose a solution for their ultimate disposal.	Since the preliminary POPs pesticides and pesticides waste have been detected at location of different generators (farms, individuals, institutes, industry etc.), it is necessary to assemble an detailed inventory of waste pesticides for one, selected district, which would serve as a general example for proper waste pesticides inventory assembling, but also for demonstrating and optimizing awareness process. This detailed inventory is necessary to be prepared according to the preliminary inventory experience and using FAO PSMS (Pesticides Stockpile Management System) with Server based data management system. FAO PSMS include: Risk assessment system and prioritization and selection of temporary storage and collection centers; Determination of quantities of POPs pesticides, obsolete pesticides, contaminated empty containers and other related materials like contaminated building materials, contaminated spraying equipment, contaminated soil and standard reporting based on lists generated by the PSMS.
Action 1.5: Demonstration Project: Management	Demonstration project will have a learning effect for Serbia on how to deal with a POPs pesticides production from the first step till final clean-up. The project will serve as learning case where authorities can learn how to deal with investigation methods, risk

POPs pesticides waste and stocks at previous POPs Production Facility.	assessment, remediation/treatment techniques, remediation plans, tender documents for clean-up, calls for tender. Also the project will serve as a learning case for the Serbian pesticides producing industry in how to deal with their production sites in the future.
Action 1.6: Assemble national-wide inventory of waste pesticides, POPs pesticides and pesticide packaging detected in Serbia.	Based on the good practice obtained through implementation of a pilot project, assemble inventories for other districts and estimate a possibility for temporary storage establishing, analyzing characteristics of the existing storage facilities in those districts, as well as detected quantities of pesticide waste. Accordingly, for specified short-term needs and find quantities of obsolete pesticides it would be useful to select one or several of the existing pesticide storage facilities to be adaptated in accordance with environmental protection requirements and other pesticides.
Action 1.7: Demonstration how to solve problem of pesticides waste from private households.	Obsolete POPs pesticides waste and other pesticides waste for private households should be dealt with in a different way from the stores and similar to the as practice in EU member states for the collection of empty containers. In the awareness campaigns, information can be spread by advertisements, leaflets and TV spots and other media. This demonstration test can also give information on expected quantities being forwarded by the private households.
Action 1.8: Demonstration: repackaging and storage of pesticides waste in one district and destruction tests in Serbia.	Demonstration should be organised at one district. Collected obsolete pesticides have to be repacked and stored at temporary store; Preparation of Demonstration Plan for final elimination by destruction in Serbia (look into local destruction possibilities in cement kilns); Public awareness campaign about understanding of technologies for waste treatment and disposal. Transfer of available destruction technologies and experiences to Serbia Transport of repacked obsolete pesticides to "demo-cement plant" if is concluded in demonstration plan as appropriate technology; Arrange 2 different trial burns for destruction of: empty packaging at cement kilns, obsolete pesticides in cement kilns. Project includes public participation and strategy to gain trust, make technologies and monitoring results more understandable to public (see therefore under Public Informing, Awareness-raising, education Strategy and Action Plan for strategy implementation).
Action 1.9: Development of Operational Plan (OP) for pesticide waste, POPs pesticides and pesticide packaging collection for substances recorded during the Actions 1.4 and 1.6, for each district nationwide defining the conditions required for carrying out related transport to destruction plant or export.	The plan is developed based on the data provided in the inventory assembled within the Actions 1.4 and 1.6. The plan addresses collection, packaging and transport of detected pesticide waste for the purpose of waste destruction in Serbia (depending on the results of Action 1.8) or export for final destruction to a waste treatment facility in the EU. OP should consider if waste should be collected into one storage facility or its collection should be organised via temporary storage. This issue will be dealt with in the demonstration repackaging under action 1.8. and the results from the inventories will have a major impact on the strategy and the number of temporary storage to be designated.
Action 1.10: Adaptation of temporary storage, facilities or facilities for storing pesticide waste, POPs pesticide and packaging whose owner is not known (not determined) and which have been detected during	In the Republic of Serbia there are currently no storage facilities where waste pesticides could be stored. Since potential storage facilities, that could be used for pesticide waste storage, have been considered during activities carried out within the scope of the Action 1.4 and 1.6., one or more storage locations should be selected to be used for storing hazardous waste whose owner is not known. Beside technical characteristics of the storage facility, possibilities for change of its functionality i.e. intended use should also be considered. All necessary administrative procedures should be conducted (obtain required permits and similar), aimed to provide the use of considered facility/facilities for pesticide waste storage. After procedures are finalised, adaptation of the facility may begin. Here considered pesticide waste storage facilities may also be used for storing other hazardous waste whose owner is not known.

inspection.	*Further the definitive number of stores will depend on the volumes of waste pesticides found in the inventory.
Action 1.11: Destruction in Serbia or export of detected quantities of POPs, other pesticide waste and POPs and pesticide packaging for the purpose of their ultimate disposal in approved/authorised facilities, in accordance with the provisions of the Basel Convention in case of export.	All pesticide waste quantities found in the inventories, as specified under Actions 1.4.and 1.6., are declared to be hazardous waste, all quantities should be collected and destroyed in Serbia or when destruction in Serbia is not possible, be exported for the purpose of their ultimate disposal at approved/authorised facility in accordance with the provision of the Basel Convention. A registered company, planned to carry out the export of pesticide waste, should be selected by a competitive public bidding procedure. According to experience from other countries and experts judgment it is estimated that the 220 tons represents about 20% of the total amount of obsolete pesticides in Serbia.

2. System for identification and sound pesticides packaging waste and pesticides waste management for future pesticides waste quantities and new empty pesticides containers established	
Action	Description
Action 2.1: Develop a system, organize capacity building, develop regulatory and financial measures for pesticides packaging waste.	System for sound pesticides packaging waste should be based on recent experiences and best practice in EU countries. An exchange programme including review study will be implemented to optimize this process. It is necessary to bring together all stakeholders that deal with empty containers and work towards by establishing a national organisation for the handling of empty pesticides containers and other packaging management. Goal is that pesticides branch takes responsibility for packaging from the cradle to grave. Also it is necessary to ensure participation of all stakeholders and sufficient financial support from all stakeholders to set up system. Important condition for success is that in Serbia, a technical solution is created at the earliest possible stage, for the recycling/destruction of the packaging materials. (It is proposed in Action 1.8 to make tests for destruction of rinsed empty containers could be made at cement kilns.) Also the following regulations define a requirement for rational packaging handling: Law on Packaging and Packaging Waste, Law on Waste Management, Law on Plant Protection Products. Subsequently, appropriate sub-legal regulations should be developed which would more precisely regulate the issue considered. Within the development of system it is necessary to create financial mechanism for empty pesticides container management. Awareness campaign for the agricultural sector should be consider, plan and performed as necessary step within the development of appropriate system.
Action 2.2: Develop a system, organize capacity building, and develop regulatory and financial measures to avoid and recurrence of obsolete pesticides.	FAO PSMS (Pesticides Stockpile Management System) with Server based data management system should be introduced in Serbia with appropriate regulatory, administrative and financial measures. The system can be based on bar coding for new containers from Serbian producers and for those entering the country at customs. Following aspects will be included: Inventory (stores and containers in use): Registration of pesticide uses: Movement instruction and tracking: Usage planning and monitoring, returns: Loss/damage reporting: Stock checking: Reporting.

	Parallel with this activities it is necessary to perform Programme for improvement of farmer management by education on: Waste, soil and water management: Store management: Integrated Pest Management: Certification of farmers practise (for example periodical sprayer controls and certication): Good Agricultural Practise (GAP): Reference manuals are dealt with under Action 2.3.
Action 2.3: Develop reference manuals for pesticide waste and waste pesticide packaging management.	In accordance with a complex issues related to POPs, pesticide waste and waste pesticide packaging management, it is necessary to organise waste handling training programmes and develop reference manuals intended for waste generators, but also collectors, carriers and operators. Specified training programmes should be correlated to training programmes considering proper management of plant protection products. It is necessary to develop: brochures explaining the rules for proper pesticide handling and storage, guidelines for the use of plant protection products, handling empty packaging and pesticide waste, guidelines for waste minimisation, intended for farmers.
Action 2.4: Assemble the inventory of POPs and other pesticides.	Based on the PSMS data type and way of data collecting, defined maintain an inventory of POPs and other pesticides. In cooperation with the Serbian Environmental Protection Agency it is necessary to define the type of data, sources and manner of data collecting for the purpose of waste pesticide data base developing.
Action 2.5: Develop reports on pesticide waste and POPs pesticides, to be submitted to the European Environmental Protection Agency and the Secretariat of Stockholm Convention.	In accordance with the Stockholm Convention, as well as for the purpose of reporting to the European Environmental Protection Agency, it is necessary to prepare a report on the current situation with respect to waste and POPs pesticides. The report should provide data drawn from PSMS on quantities of pesticide waste and POPs pesticides, as well as data on the quantities of waste pesticide and POPs pesticide packaging.

Horizontal Action plans considering institutional and regulatory measures aimed at Stockholm Convention implementation and reporting, Action plan considering monitoring; Action plan for contaminated areas and development; Strategy for public informing, awareness raising and education and action plan for strategy implementation describes actions required for POPs pesticides management as well.

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Section 4: Obsolete pesticides and POPs – destruction technologies

RADICALPLANET TECHNOLOGY (RPT): ALTERNATIVE FOR INCINERATION OF OBSOLETE PESTICIDES

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Abstract

Radicalplanet technology is the complete detoxification method which changes chemically obsolete pesticides into safety compounds in closed vessels by using the mechanical high-energy, under the conditions of non-combustion. The pure obsolete pesticides (in the state of solid and liquid) and PCB were treated, as with all the admixture contaminated by POPs wastes (concrete brocks, soil, glass, steel can and pipes, plastics, protective clothing and gloves, chipped wood, card board paper and so on). There was no fear of secondary pollution, because this process is guaranteed such clean conditions as non-exhaust gas and non-effluent. The CaO bricks, safe and less expensive additives, were utilized for de-chlorine agent; pure-DDT(1kg)+CaO(0.39kg)=$CaCl_2$(0.78kg)+Non-chlorinated organic-compounds(0.61kg). The toxic equivalent value became below 1 pg-TEQ/g and the destruction removal efficiency (DRE) was over 99.9999%. The electric cost was estimated at approx 3600 kW-h/t. This Radicalplanet Technology was officially granted in April 1ST, 2004 in Japan. This system is put into practical-use now. The vessels' inner-volume of A-500 Type Machine is 1,500 liters. And the calculated capacity of this A-500 Type is approx 680 ton-Pesticides/year/1-machine. This practical system will be installed on site. And these equipments will be carried by trailer. Any project in the world may operate the E-200 Type Machine (Practical Demonstration Size) on lease, ahead of the full scale treatment.

Key Words: mechanical energy, non-combustion, non-exhaust gas, non-effluent, Detoxification, POPs wastes, Obsolete Pesticides,

Technology description[1), 2), 3)]

The fundamental principle of Radicalplanet Technology is follower that the organochlorinated pesticides (OCPs) are converted into the safety non-chlorinated organic compounds by interacting with CaO bricks. Organo-chlorinated compounds are obsolete pesticides, chemical wastes, PCB and so on. The additive is CaO and by-product is $CaCl_2$. The driving force is not incineration but strong mechanical energy. The detoxification reaction is occurred in the tightly-sealed vessel under the non-combustion condition. Hence non-exhaust gas and non-effluent are generated in the period of the detoxification reaction.

In concrete forms, there are steel balls, CaO bricks and pesticides, such as DDT, in the secure steel vessel. Steel balls crush hard each other by strong impact energy. The chlorine molecules are cut off from the organic compounds. Then the all activated chlorine molecules react chemically with activated CaO and become to safety inorganic compounds ($CaCl_2$).
Pure-DDT(1kg)+CaO(0.39kg)=$CaCl_2$(0.78kg)+non-chlorinated organic-compounds(0.61kg).
This chemical reaction is environmentally guaranteed clean and safe conditions. Additionally this process can be used for not only chemical wastes but also admixture contaminated by POPs wastes such as obsolete pesticides, PCB and Dioxin. Powdered particles are produced after the detoxification reaction finished. $CaCl_2$ in the powder dissolves in water. The extracted $CaCl_2$ is re-used for inorganic chemical materials such as Calcium Apatite. The non-

chlorinated organic compounds remained as residue. These are re-used for the chemical materials and can be burnt up completely without generating Dioxin.

Performance[1)] (Practical demonstrations of the E-200 type[1)] machine)

E-200 type machine with normal capacity of 0.9-1.1 tonnes of chemical pesticides per day was selected for the practical demonstration process. The inner volume of solid vessels was all in all 750 liters. The size of the E-200 type is approx 4m(L)×4m(W)×4.5m(H).

(1) Targets of performance:

(a) Chemical wastes: All chemical wastes were offered by Ministry of Agriculture, Forest and Fisheries (Japanese Government). BHC powder was in card boxes and BHC petroleum emulsion was in grass bottles. DDT powder was in card boxes. PCP solution was in glass bottles. Chlordane petroleum emulsion was in glass bottles. Endrin powder and PCNB powder were respectively in card boxes.

(b) PCB wastes: PCB was transformer oil contained Pure-PCB(51.3%)+Tri-Chloro-Benzene (38.4%) in glass bottles. Stabilizer had approx 2%Pure-PCB. Admixture was contaminated with approx 0.2%Pure-PCB. Soil was contaminated with 4.28%Pure-PCB.

(c) Ash and Soil polluted by Dioxin: Ash was collecting from an incinerator and Soil was collecting from the surrounding area of the incinerator. Toxic Equivalent of Dioxin was 6900 pg-TEQ/g in Ash and was 8200 pg-TEQ/g in Soil. The polluted soil was offered by Ministry of Environment (Japanese Government).

(2) Process diagram: (a), (b) and (c)

(a) Chemical wastes (target wastes of POPs) were put into each solid vessel with steel balls and CaO bricks. Excess CaO (called “Angelic Quick Lime”) was practically put into the each vessel in order to promote the speed of detoxification reaction and to get the perfect de-chlorination reaction. After then these vessels were capped and sealed tightly.

(b) E-200 type machine was operated and detoxification reaction started. The speed of the vessel rotation and the base revolution was controlled 70 rpm concurrently. Detoxification time was complete in approx 3.0 hours.

(c) After treatment, these vessels were opened and the final safety powdered particles were taken off by collecting equipments. This process was operated in the closed system in order to keep the operators on the clean conditions. When the vessels were opened, powdered particles were never flied apart. The vessels and steel balls were used on the next treatment.

The conditions of detoxification reaction were different from each operation, for example, the treating time, the quality and amount of chemical wastes in each vessel and so on. The results of practical demonstrations were shown in table 1.

The permission to apply the “Radicalplanet Technology” was officially granted by the Notification No.25 (April 1ST, 2004) of the Ministry of Environment in Japan regarding “The Law of Special Detoxification Technologies on PCB (and POPs) Wastes”.

Preparation of full scale practical treatment by A-500 type main machine

Based on these results, A-500 type machine is prepared for full scale practical treatment. The inner volume of solid vessels is all in all 1500 liters. The speed of the vessel rotation and the base revolution can be concurrently controlled 70-100 rpm. The speed of de-chlorination

Table 1. Results of Detoxification in Practical Operation[2), 3)]

Chemical Wastes	Total Weight (kg)	After-treatment Dioxin+Co-PCB (pg-TEQ/g)	DREs and DEs
97%BHC <p> 5%BHC <p> 3%BHC <e>	12 28 15.6	□1 (Min.0.31) □1 (Min.0.14) □1 (Min.0.38)	DREs□99.9999% DEs□99.99%
5%DDT <p> 2.5%DDT <p>	18.5 5.2	□1 (Min.0.08) □1 (Min.0.18)	
2%Endrin <p>	2	□1 (Min.0.28)	
91%PCP <s>	12.6	□1 (Min.0.18)	
42%Chlordane <e>	12.6	□1 (Min.0.034)	
95%Chlordane <e>	3.5	□10 (Min.6.2)	
20%PCNB <p>	2	□5 (Min.0.54)	
DDT+Endrin+BHC <mixed-p>	7	□1 (Min.0.12)	
Undiluted (Transformer) PCB <o>	342	□1 (Min.0.004)	DREs□99.99999% DEs□99.999%
Stabilizer (2%PCB) <o>	10	□1 (Min.0.00027)	
Admixture (0.2%PCB) <o>	90	□1 (Min.0.0018)	
Polluted Soil (4.28%PCB) <o>	125	□1 (Min.0.004)	
Incineration Ash (Dioxin)	180	□1 (Min.0.012)	DREs□99.9999% DEs□99.99%
Polluted Soil by Dioxin	200	□1 (Min.0.012)	
<p>:powder, <e>:emulsion, <s>:solution, <mixed-p>:mixed powder, <o>:oil			

reaction becomes twice or four times. Then detoxification treating time is complete in approx 1.4 hours and one cycle time is approx 2.4 hours. The normal capacity of A-500 type machine is approx 1.8-2.1 tonnes of chemical pesticides per a day. The capacity increases to approx 10-12 tonnes per a day in cases of soil and concrete blocks contaminated by chemical wastes. Estimated standard capacity and electric cost in A-500 type are shown in Table 2. Usually two machines are operated in alternate shifts in order to practice effectively. In the actual full scale process diagram, the process (d) and (e)-items will be added to (a), (b) and (c).

Table 2. Estimated Standard Capacity and Electric Cost in A-500 type (One Plant)

Chemical Wastes	Density (ton/m^3)	Amount (kg/Charge)	Treatment Time(hr)	Cycle Time(hr)	Capacity		Electric Cost(kW-h/t)
					(t/day)	(t/year)	
Pesticides-A(s)	2	214	1.4	2.4	2.1	677	3,600
Pesticides-B(l)	1.5	160	1.4	2.4	1.7	5.9	4,810
PCB-Oil (l)	2	75	2.0	3.0	0.6	190	14,670
Stabilizer (s)	3	113	2.0	3.0	0.9	284	9,730
Polluted Soil	3	1,125	1.4	2.4	11.4	3,555	684
Operation Time: 24 hours in a day, 316 days in a year. (s) is solid, (l) is liquid							

(d) $CaCl_2$ can be separated from the final safety powdered particles by dissolving in water. The non-chlorinated organic-compounds remain as the residue including $Ca(OH)_2$.

(e)-1. Organic compounds can be dissolved out some useful organic ingredients from the residue with suitable solvent. Hence a little amount of $Ca(OH)_2$ remains as the residue.

(e)-2. Organic compounds can be burned completely without generating Dioxin. In this process, $Ca(OH)_2$ becomes to CaO with releasing water, and is re-used as “Angelic Lime".

(e)-3. When the content of pesticides wastes is dilute, 0.1-1%, blast-furnace slag is considered appropriate for Angelic CaO. After the process (d) and after the processes (e)-1 or (e)-2, the residue becomes to quite hard concrete materials such as $400kg\text{-}f/cm^2$ in strength.

Any project must add a process (d) and choose the process from (e)-1, (e)-2 or (e)-3 in the full scale treatment. The practical full-process shows Figure 1, which is chosen (e)-2.

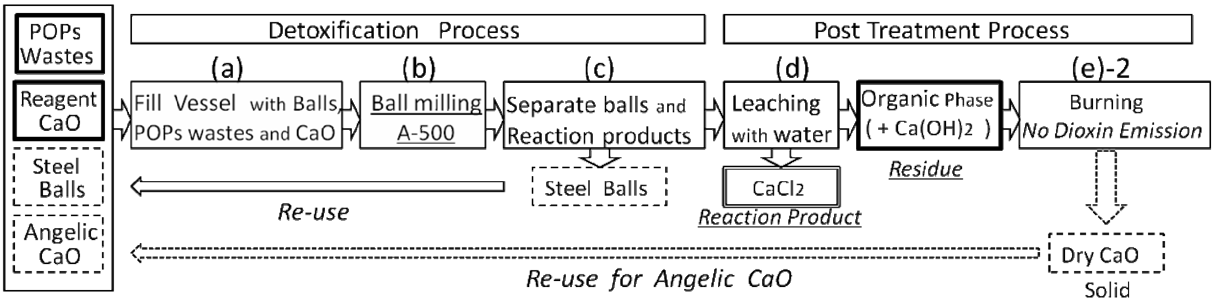

Figure 1: The Example of the Practical Full-Process

Criteria on the Adaptation of the Country to the Technology[2), 3)]

(1) Resource needs

(a)Electric power source: A-500 type machine is prepared for full scale practical treatment. The power source is AC440V, 3φ, 60Hz. Electric motor is equipped with 500kVA×1000rpm and the powder collection equipment is operated by AC 220V, 30kW.

(b) Water requirements: Main machine requires cooling water, 10 liters/min, which is stocked in the 10 m3 tank and is continuously recycled through the heat exchangers.

(c) Gas volumes: Neither gas nor fuel is consumed in the detoxification reaction, because the Radicalplanet Technology is non-combustion and closed system. After treatment, air or inert gas will be used for collecting and carrying the safe powdered particles.

(d) Reagent volumes: CaO bricks are used for the de-chlorination reagents. The theoretical amounts of reagents are, for example, approx CaO(0.39kg) per pure-DDT(1kg). Angelic CaO, excess CaO, was added by approx 20 % of theoretical CaO, in order to promote the chemical reaction. When the concentration of chemical wastes is not cleared, Angelic CaO is increased by approx 50% over in order to keep safe for the complete detoxification.

(e) Weather tight buildings: Weather tight buildings are required but have to be ventilated, because the main treatment plant and working field will be required to be protected from the rain, strong wind and the direct sun-shine.

(2) Costs:

(a) The main plant (A-500 type) and surrounding equipments: Any project in the world can select from among several options, buying or leasing, and can practice the E-200 type machine (Practical Demonstration Size) on lease, ahead of the full scale treatment by A-500 type machine. Usually it takes about 15 months to produce A-500 type plant, but E-200 type machine and surrounding equipments are already build-up.

(b) Electric costs: Main electric cost is approx 3600kW-h per ton of chemical wastes (=540kW×1.4h/214kg).

(3) Risks

(a) Risks of reagents applied: CaO bricks are applied for de-chlorination reagents. CaO bricks are quite safe reagents, are widely used in home and in industries and well managed.

(b) Risks of technology: No risks. The practical scale machine E-200 type was already operated in Japan, and by which this technology was officially granted by Notification of Japanese Government, on April 1ST 2004. And the polluted materials never expand, because this technology is a closed system and never generate the exhaust gas effluents during the detoxification reaction.

(c) Operational risks: No risks. At the state of emergency, such as the earthquake and the natural phenomena, the main plant is stopped safely, immediately, automatically and completely. After the finishing of emergency, the system can be continued to operate again safety. During the stopped periods, the operating vessels are kept to be closed tightly.

(4) Constructability:

(a) Ease of installation/construction of main plant and surrounding equipments: It is easy to construct the treatment plant. It takes about one month.

(b) Optional process equipments: *Pre-treatment:* When the wastes are stored by large size of drums (200kg) and vinyl bags (500kg), the suitable re-package equipment will be required in order to make a handling size of vinyl bags (10-20 kg) or of small cans (10-20 liters) and to keep the labors from hazardous conditions.

Post-treatment: All projects should decide the post-treatment processes of (d) and (e)-items. Equipments of post-treatment are different. In process (d), a water leaching equipment is prepared. In (e)-1 process, solvent-extraction equipments are prepared. In (e)-2, a little burning equipment is prepared. When (e)-3 is chosen, casting equipments are prepared in order to knead and cast the mixed powder of CaO, SiO_2 and Al_2O_3 by with water. This casting concrete becomes quite hard by addition of only water and by pressed.

(c) Ease of shipping/transit: The main machine is simple, compact and transportable by trailers from country A to country B. And the machine can be separated into two pieces.

(d) Ease for operation: Labors can operate easily A-500 type machine by on and off. The main jobs of operators are to put the chemical wastes bags into each vessel safety and to set the each vessel on the machine steadily. After treatment, the jobs are to set off each vessel from the machine and to collect the powdered particles from each vessel by use of suitable equipments.

Conclusion

Radicalplanet Technology (RPT)[4)] will be best in alternatives for incineration of obsolete pesticides, and particularly have some aspects of these alternatives related to environmental impact, cost, practical value and using on site.

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MANAGEMENT OF PESTICIDE AND POLYCHLORINATED BIPHENYL WASTES FROM THE PACIFIC ISLAND COUNTRIES FOR DESTRUCTION BY COMBINATION OF THERMAL DESORPTION AND PLASMA ARC TREATMENT

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Persistent organic pollutants such as polychlorinated biphenyls, organochlorine pesticides and organophosphate pesticides were imported into the Pacific region to assist development of island economies. The use and subsequent legislative control of persistent organic pollutants led to stores of waste pesticides and polychlorinated biphenyls throughout the Pacific.
A waste management program was commissioned by the Australian Government to clean up these chemicals in the Pacific Region. This program was known as Persistent Organic Pollutants in Pacific Island Countries (POPs in PICs). The program ran between its inception in 1997 to 2009 whereby the collaboration of the Australian Agency for International Development (AusAID), the South Pacific Regional Environmental Programme (SPREP), GHD Pty Ltd, the Hatlar Group Pty Ltd, HK Logistics and BCD Technologies Pty Ltd resulted in the successful waste identification, auditing, packaging, collection, transport and destruction of the chemical and chemically contaminated wastes.
The waste was transported from Pacific Island countries to the BCD Technologies facility in Brisbane Australia. The destruction of the waste utilised a combination of treatment processes including Indirect Thermal Desorption and Plasma Arc destruction by the Plascon® technology. In total, one hundred and twenty three tonnes of waste from eleven Pacific Island countries has been relocated to BCD Technologies waste treatment facility and destroyed in a manner that typically achieved destruction efficiency of greater than 99.9999%

Australia is the largest and closest developed country in proximity to the Pacific Island region Countries. Historically, Persistent Organic Pollutants (POP's) such as polychlorinated biphenyls (PCB's), organochlorine pesticides (OCP's) and organophosphate pesticides (OPP's) were imported into the Pacific region to assist development of island economies. Pesticides were used in agricultural activities and electrical equipment containing PCB oil in the form of transformers and capacitors were used to support light industries and power generation. Air-borne application of DDT was used to manage malaria-bearing mosquitos. Many of the imported pesticides and herbicides were never used and were often stored in environments that allowed the products and packaging to deteriorate, contaminating the immediate environment. This led to stores of waste POP's throughout the Pacific.
Most Pacific countries are small island developing states (SIDS), which lack the specialised resources such as technology, power and economy needed for treatment and disposal of POP's. Lack of awareness of the hazardous nature of these chemicals and poverty contribute to the unsafe storage of many of these chemicals. This risk of human exposure and environmental contamination led to an initiative by the Australian Government to clean up POP's in the Pacific Region. This program was known as Persistent Organic Pollutants in Pacific Island Countries (POP's in PIC's).

Identification, Packaging and Transport of the Pacific Islands Waste

The Australian Government, through the Australian Agency for International Development (AusAID) and in cooperation with the South Pacific Regional Environmental Programme

(SPREP), undertook a pre-feasibility study of potential waste management projects in the Pacific region in 1997. AusAID identified the safe removal of POP's wastes to an international destruction facility as the most urgent project. As a result, funding was provided to develop a project to identify, repackage, remove and destroy the legacy intractable waste from the Pacific Region. These wastes were identified primarily as those chemicals listed under the *Stockholm Convention on Persistent Organic Pollutants.* The project also included other pesticides with similar characteristics of persistence in the environment. The project was broken in to two phases;

Phase I of this work was to conduct assessments of stockpiles of obsolete chemicals and identify contaminated sites in each of the thirteen participating Pacific Island Countries. The countries selected to be involved in the project included Cook Islands, Federated States of Micronesia (FSM), Fiji Kiribati, Marshall Islands, Nauru, Niue, Palau, Samoa, Solomon Islands, Tonga, Tuvalu and Vanuatu. Phase I also identified a number of contaminated sites and waste storage locations within the participating Pacific Island Countries. These ranged from sheds housing deteriorating packaged pesticides to outdoor enclosures housing leaking PCB contaminated electrical equipment. In many instances the storage locations for these wastes were also contaminated, thus including contaminated soil and infrastructure.

Phase II of the POP's in PIC's project was managed by GHD Pty Ltd (GHD) (project management), in coordination with SPREP (regional liaisons and auditing), The Hatlar Group (waste management), HK Logistics (shipping logistics), BCD Technologies (waste destruction) and partner governments in the region.

Initial Reconnaissance and Assessment

An initial reconnaissance visit was conducted on each island to inspect identified storage sites, to confirm contents and volumes of all chemicals, and conduct any field-testing or sampling required. If the composition of chemicals was unclear, samples were collected and sent to Australia for analysis.

Clean Up and Re-Packaging

GHD's cleanup team re-visited each of the countries to complete collection and repackaging of POPs stores. In some instances, additional chemicals were also identified due to increased public awareness about POPs as part of the project. Due to the island topography and resources and the need to import all packaging materials and equipment, the collection of POPs was generally undertaken manually. The chemicals and contaminated soils and materials were repackaged into 205L UN Certified drums unless, in the case of electrical transformers, this was not practical. Electrical transformers were drained of oil and separately packaged in freight containers. Absorbent material was used inside the transformers to soak up any residual oil and the transformer casings were wrapped in plastic prior to shipping. All packaged materials and freight containers were labelled with both dangerous goods and project identification labelling for shipping. This information was documented on a detailed manifest. Involvement from local government and local workers in the packaging and manifesting further increased the awareness of hazardous materials in the region.

Import Approvals and Shipping

Special waste import permits are required to transport hazardous waste in to Australia. The Waigani Convention and Basel Convention are the basis for these permits which were issued by the Australian Department of Environment and Heritage, Water and the Arts (DEWHA). Legislative compliance and the success of the importation process was due to development and implementation of a comprehensive communication strategy that established relationships and trust with key stakeholders such as local community groups, shipping unions and environmental groups in Australia.

POPs were shipped from the Pacific Islands to the Port of Brisbane, located in south-east Queensland, Australia. The containers were inspected by Australian Customs and the Queensland Environmental Protection Authority upon arrival. At the end of 2005, shipment of the waste to Australia commenced from Samoa, Fiji, Tonga and Cook Islands. Shipping logistics and scheduling were a major challenge on this project, and were managed by flexible scheduling and frequent communication with stakeholders.

<u>Waste Management for Destruction</u>

BCD Technologies was the receiving facility for the POP's in PIC's waste. The facility, based in Brisbane, Australia was the only facility in Australia that was both licensed and capable of managing the complex contaminated waste streams presented by the POP's in PIC's project. The combination of this capability and the proximity to the Pacific Islands meant the waste would travel the least distance and would not require further separation of waste streams to different treating facilities.

The key to successful management of the POP's in PIC's wastes for destruction from 2006 was a combination of materials handling and specialised waste treatment technology. This was achieved by utilising the manifest information supplied by GHD to schedule containers of similar waste types to enable a waste management focus on scheduled blocks of similar work.

Once the containers were opened the wastes were identified for waste processing drum by drum. Broadly the waste ranged from easily manageable quite "clean" wastes such as electrical transformers and the oil from these, to severely co-contaminated wastes. The terminology "clean" means that the waste was not mixed with other contaminants or other matrices. By contrast the co-contaminated wastes included drums of concentrated DDT pesticide powers mixed with contaminated soils, drums of liquid solvent-based pesticides, contaminated plastic and metal packaging, wooden items and any materials that had come in to contact with the waste such as protective equipment and wood from huts and pallets.

Clean low-PCB concentration transformer oils were treated through the base-catalysed dechlorination (BCD) process in use at BCD Technologies. All the remaining materials required treatment through Plascon$^{(R)}$ for liquid materials or pre-treatment through an Indirectly Heated Thermal Desorber (ITD) for solid contaminated items prior to treatment of the collected condensate through Plascon$^{(R)}$.

Indirect Thermal Desorption (ITD)

The ITD plant utilised at BCD Technologies Narangba facility is a purpose built batch process designed for removing oil from contaminated electrical equipment such as capacitors and transformers. The receipt of a broad range of contaminated items and a number of solid pesticides and pesticide contaminated items meant a review of the operation of the ITD plant was necessary. Although the plant was not designed to accommodate these additional waste streams it ultimately proved to be very effective at managing them. When treating pesticides through the ITD plant, a number of engineering and administrative modifications were required. For instance, pesticides generally condense as solids rather than liquids as PCB's do, and, since pesticides are typically in non-conductive media such as powders and soils the surface area of the waste to be treated had to be increased. This meant aspects related to both the waste delivery into the plant and waste exit from the plant required engineering modification, to increase surface area while maximising throughput and avoiding pipe blockages at the outlet points of the main chamber. The recipes' for the batch process were also modified providing variable temperature escalation platforms as pesticides tend to have more variable boiling points than PCB's.

Outside of the operational hurdles of treating the waste the process of verification of destruction of the waste required development of analytical methods through a gas chromatograph coupled with a mass spectrometer. The ability to conduct analysis on site meant operational decisions could be made on the same day the waste was treated. The residual amounts of POP's in the treated solid wastes were verified below the Australian landfill acceptance criteria limits of 50 milligrams per kilogram (mg/kg) for the cumulative total of each of the compounds within the chemical families of PCB's, and pesticides respectively. Additionally independent samples of the treated solid waste material were taken by GHD and sent to an external laboratory, which provided comparable results to those obtained at BCD Technologies.

PCB oil used as a solvent in the collection tank connected to the ITD plant dissolved both pesticide and PCB contaminants boiled off during the process. The resultant liquid mixture was filtered and separated in to its aqueous and oil components for treatment through Plascon®.

Plascon®

The Plascon® technology was developed in the early 1990s specifically to destroy chlorophenoxy waste from 2,4-D herbicide manufacture. From the mid-1990s, BCD Technologies employed a Plascon® for destruction of halon fire extinguisher and CFC refrigerant gases, as well as more recently HCFCs and synthetic greenhouse gases. BCD Technologies commenced treating PCB oils through a Plascon® plant in the late 1990s.

The principle behind the operation of Plascon® is a two-stage process of achieving temperatures hot enough to generate conditions of pyrolysis for any waste in contact with the plasma followed by rapid cooling of the waste gases to prevent formation of dioxins and furans.

Stage 1, heating, is achieved by generating an argon plasma arc at over ten thousand degrees celcius utilising a 150kW direct current arc (the plasma torch). This is coupled with a specially designed injection manifold that introduces the liquid waste directly into the plasma. This specially designed manifold means that the minimum waste destruction temperatures are around three thousand degrees Celcius. The pyrolysis conditions achieved at these temperatures result in any pesticide or PCB molecule in contact with the plasma completely dissociating in to individual atoms and ions. The resulting gases pass through a reaction chamber, falling to around one thousand degrees celcius over approximately three milliseconds.

Stage 2, cooling, is achieved by passing the gases through an aqueous alkali scrubber over approximately 15-20 milliseconds reducing the temperature to under one hundred degrees Celcius. This rapid temperature drop is designed to avoid the temperature ranges over which dioxins and furans form. For treatment of the POPs in PICs waste GHD conducted independent air quality monitoring of the Plascon® process which showed dioxin and furan emissions at less than the Australian guideline value of 0.1 nanograms per cubic metre of air emissions (0.1ng/m^3 TEQ).

As the POP's contain chlorine molecules, hydrochloric acid forms from the pyrolysis products. The alkaline quench neutralises these acids to a salt solution which is discharged as a trade waste to sewer. Because the POP's and the oils and solvents they are dissolved in, contain carbon, oxygen is added to the reaction to promote the formation of carbon dioxide and thus prevent solid carbon formation within the Plascon® pipe-work. This gas is discharged to atmosphere. Both the discharge to sewer and emission to air are monitored for residual POP content. The most recent testing by GHD in January 2009 returned the following environmental emission results while treating almost pure (100%) PCB oil;

Contaminant	Type Of Emission	Test Results (Concentration)	Australian Concentration Guideline Value	Units/Notes
Polychlorinated Biphenyls	Air	0.4	1.0	ug/m^3
	Water	<0.1	2.0	ug/L
Dioxins and Furans	Air	0.0055	0.1	ng/m^3 TEQ
Destruction and Reduction Efficiency (DRE)	Overall	99.999998%	99.99995%	(BCD Technologies license Limit)

The challenges in treating PCB's and pesticides from the POPs in PICs project were mostly related to feed preparation, engineering modifications to allow feeding of liquids of different density and viscosity and improving environmental management safeguards to ensure compliance during plant start up, shut down and in event of equipment failures.

The Plascon® plant has proven capable of achieving destruction and reduction efficiencies for both PCB's and organochlorine pesticides in excess of 99.9999%. Other waste types treated by Plascon® include pefluorooctanylsulfonate (PFOS), chlorinated solvents, modern pesticides, halons, hexachlorobenzene, CFC's, HCFC's, HFC's and PFC's and SF_6.

The POPs in PICs program managed by GHD Pty Ltd in conjunction with AusAid showed how a mixture of very different POP contaminated waste types could be safely classified, packaged, transported and destroyed. The opportunity to be involved in this project provided BCD Technologies a complex challenge through which the company learned to utilise its specialised technology. Specifically BCD Technologies gained valuable experience in separating incoming waste and modifying waste treatment processes to treat each waste stream in an environmentally sound manner.

TREATMENT OF HCH MATERIALS BY THERMAL DESORPTION AND NANO-CATALYSIS

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Abstract

We present laboratory and pilot-plant data for evaluating the on-site treatment of HCH-contaminated materials from a European landfill. The landfill contains about 170,000 tons of material contaminated with HCH at concentrations < 5,000 mg/kg and about 6,000-14,000 tons of HCH at concentrations ranging from 20-50 %. The evaluated process consists of indirect thermal desorption and catalytic treatment with nano-iron catalyst. Samples were obtained by excavating portions of the landfill and composited. Desorption of HCH was effective at 400^{o} and led to the partial formation of chlorinated benzenes and polychlorinated dibenzodioxins and furans (PCDD/PCDF). HCH and the by-products were decomposed effectively at 300^{o} in the presence of oxygen and nano-iron oxide catalyst. Process design identified waste quantity, catalyst cost, and neutralization of HCl as primary cost factors. This process is suitable for the non-incineration treatment of a variety of persistent organic pollutants (POP).

Key Words

Persistent organic pollutants, POP, HCH, PCB, polychlorinated dioxins, thermal desorption, catalytic dechlorination, nano iron oxide, treatment.

Introduction

Persistent organic pollutants (POP) have been recognized as a global problem (Stockholm Convention, 2001) because of their wide-spread use, persistence, and transport. Chlorinated pesticides such as lindane (generally as a mixture of non-active lindane isomers, HCH), DDT, dieldrin, endrin, and polychlorinated biphenyls (PCB), polychlorinated dibenzodioxins and furans (PCDD/PCDF) remain as residues in soils and sludge or as high-concentration product in many countries around the globe. Many innovative alternatives to the common treatment method for POP, incineration, have been tested but have been applied at a large-scale only rarely. We have combined commercially demonstrated thermal desorption technology with new, nano-catalytic treatment of POP vapours to provide a new, non-incineration alternative to POP treatment.

Laboratory and pilot-plant testing was carried out with material obtained by excavating waste from a former European landfill covering about 50,000 m^2 containing waste to a depth of about 3-4 m. The landfill is estimated to contain about 170,000 tons of material contaminated with HCH at concentrations < 5,000 mg/kg and about 6,000-14,000 tons of HCH at concentrations ranging from 20-50 %.

Materials and Analytical

Low-concentration soil was crushed and homogenized in a blender. High-concentration material was hand-selected from the excavation, crushed, and homogenized. Analyses for

HCH isomers used USEPA analytical method SW 8081A/8082. PAH and chlorobenzenes were analyzed by USEPA 8270C and PCDD/PCDF by USEPA Method 1613. Gas streams were tested with Draeger tubes or by adsorbing on XAD resins, followed by extraction and gc/ms quantitation.

Indirect Thermal Desorption (ITD)
Indirect thermal desorption (ITD) has proved to be an effective waste reduction method over the last 15 years[1]. In this method, contaminated solids are heated indirectly in a rotating tube to 300-500 ^{o} and the volatile components are condensed. Mobile ITD units can operate effectively at 3-20 Tons/hour. Because solid particulates also carry over into the gas stream, an aqueous sludge of about 2 % of the original volume is collected and must also be disposed. So, although no flame contacts the organic pollutants, the process serves only to reduce the volume greatly. In the US, landfill or incineration disposal are general options for these residuals. This is not the case in many other parts of the world.

ITD processes have treated over 500,000 tons of PCB-contaminated soil using equipment capable of treating 10-25 tons per hour (TPH). Dioxin-contaminated soil has also been treated in ITD pilot systems[1]. This extensive large-scale experience generally is sufficient for defining appropriate operating parameters for new applications. In some cases, however, laboratory treatability testing is carried out because of the complex nature of the waste or in order to obtain specific types of information. We prefer to use the rotating tube method which uses a rotating cylinder holding about 500-5,000 g of waste. Rotation of the heated cylinder simulates the actual heat transfer that can be achieved in full-scale systems and gives data that can be scaled to large operating units. In addition, the setup incorporates a heated filter, condensing impingers, and carbon and XAD tubes for vapor collection. This method may allow an estimate of the mass balance for the process. **Figure 1** shows a schematic of the system. The contaminated material is heated to the desired temperature, maintained at that temperature for selected periods of time, and cooled.

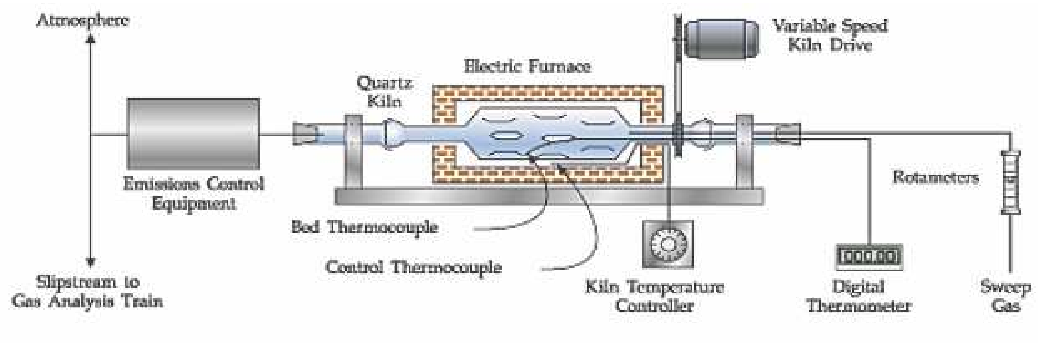

Figure 1. Schematic of Rotating Tube Mini Plant (Hazen Research)

Table 1 summarizes treatment data collected with the rotary tube mini-plant for the low-concentration, HCH material from the landfill. Condensate and gas streams trapped on XAD resin showed mixtures of chlorobenzenes, PAH, and PCDD/PCDF.

Table 1. Indirect Thermal Desorption Data for HCH-Contaminated Material at 400°

Parameter	Feed, mg/kg	Treated Soil, mg/kg
α-HCH	3,100	0.25
ß-HCH	300	0.12
γ-HCH	51	0.005
δ-HCH	37	0.014
Total HCH	3,480	0.39

These data are consistent with those obtained for other POP, shown in **Table 2**, although the type of soil may affect the relative desorption behavior.

Table 2. Indirect Thermal Desorption Data for Several POP

POP	Soil Temperature, ° C	Initial Concentration, mg/kg	Treated Soil Concentration, mg/kg
PCB	450	3,168	0.1
HCH	400	3,480	0.4
TCDD	478	0.563	0.044
PCDD/PCDF (I-TEQ)	450	4.57 μg/kg)	0.09 (μg/kg)

Nano-Iron Catalysis

Iron nano-particles dechlorinate PCB and other chlorinated pollutants efficiently [3,4]. We have recently described the catalytic dechlorination by iron oxide nano-particles of γ-lindane (hexachlorocyclohexane, HCH) and of PCDD/PCDF produced during the reaction[5].

The vapor phase pollutant was passed through columns containing the nano-catalyst, adsorbed on a ceramic foam, at 300 ° in the presence of oxygen. Synthetic lindane was fed at 12 g/hr into a heating tube operating at 250 °, followed by a dual-column system consisting of two consecutive 7-cm long ceramic plugs of 3.4 cm diameter with 7 % nano-iron in the first column, 3 % nano-iron in the second column. Lindane destructions at residence times of 5 sec could be maintained at 95-99 % over an extended series of experiments. Chlorobenzenes reduction was >95 % at the conditions of the experiments. PCDD/PCDF were reduced from 19,750 ng I-TEQ/m^3 to 195 ng I-TEQ/m^3 (>99 %). The long-term effectiveness of this process depends on the lifetime and regenerability of the catalyst with waste material.

Consequently scale-up experiments were carried out. Scale-up from the laboratory experiments focused on feed rate per volume of catalyst, column dimensions, flow rate per catalyst area, residence time, and oxygen concentration. Scale-up experiments were carried out in dual steel columns, 1 m long and 15.2 cm inside diameter. The first column contained about 2,906 g of small lentils containing about 5 % nano-iron on ceramic foam, the second column about 2,406 g. Acid gases were scrubbed in a sodium hydroxide scrubber solution. Carbon dioxide, hydrogen chloride, and carbon monoxide were formed, although a mass balance remained elusive because of experimental difficulties. Phosgene was not observed in the vapor stream. Chlorobenzenes formation and disappearance was consistent with laboratory data. At feed rates of about 1 kg HCH/hour, HCH destructions were greater than

99 % over a period of several hours. The successful scale-up of about 100 times from laboratory experiments confirms our understanding of the important scale-up parameters.

The design of the full-scale plant incorporated the results from thermal desorption mini-plants and full-scale plants, and the nano-catalyst pilot plant. **Figure 2** shows the process flow diagram for catalytic dechlorination of HCH-contaminated materials.

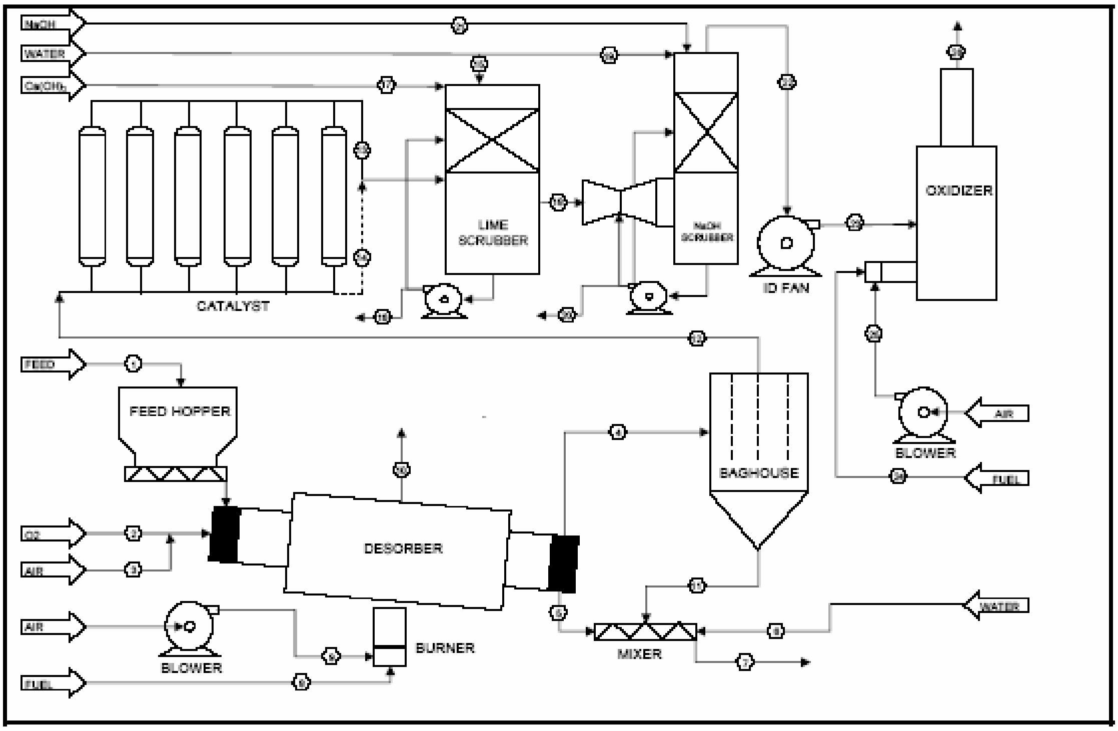

Figure 2. Process Flow Diagram for Catalytic Dechlorination of HCH-Contaminated Materials

Summary

Mini-plant data for indirect thermal desorption are consistent with full-scale data for desorption of various POP from contaminated soil. Treatment of HCH and other POP in the vapor phase was demonstrated in laboratory and pilot-plant experiments. These data allowed design and cost estimation for a full-scale process. Based on the process design, major cost factors are waste quantity and water content, catalyst cost, and neutralization and disposal of HCl (6 mol HCl/mol HCH). Costs fall into two categories:

1. Fixed costs- work plans, equipment transport and setup, mobilization, performance testing, decontamination, and demobilization.
2. Thermal operations- labor, health and safety equipment, living costs, fuel, water, electricity, chemicals, catalyst, maintenance, insurance, analyses, water treatment, and equipment depreciation.

Costs were estimated for three examples:

- A site containing 10,000-20,000 Tons of material contaminated with < 5,000 mg/kg of HCH, water content 15 %. The estimated costs are about euros 200-220/ton.
- A site containing 100,000 Tons of material contaminated with < 5,000 mg/kg of HCH. Costs are estimated at euros 130-160/ton.
- A site containing about 10,000 tons of material contaminated with 20 % HCH. Costs are estimated at about euros 400/ton.

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GPCR TECHNOLOGY APPLICATIONS AND NATURAL ENERGY SYSTEMS

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ABSTRACT

Gas Phase Reduction (GPR) is a proven technology and is well suited for the destruction of Persistent Organic Pollutants such as pesticides. This paper will discuss the application of the GPR process to HCH pesticide wastes in various waste matrices including landfills and pure chemical stockpiles. The GPR process has successfully demonstrated the destruction of pure HCB chemicals and the results of these tests, including lessons learned, will be presented.

The GPR technology and its application to the destruction of hazardous organic chemicals was invented and patented by Dr. Douglas Hallett in 1990. In February 2009, Hallett and McEwen submitted a new patent with the United States Patent Office entitled PROCESS FOR THE CONVERSION OF ORGANIC MATERIAL TO METHANE RICH FUEL GAS. The new patent builds on the technology of the first patent, optimising the conversion of organic waste to a hydrogen enriched methane gas that is suitable for a variety of applications including fuel for vehicles and the generation of electricity.

Natural Energy Systems was incorporated to develop the new business model surrounding the latest patent and to promote the GPR technology and the conversion of organic waste to energy. The concept of building a Municipal waste to energy plant that also has the ability to destroy POPs wastes will be discussed.

KEY-WORDS

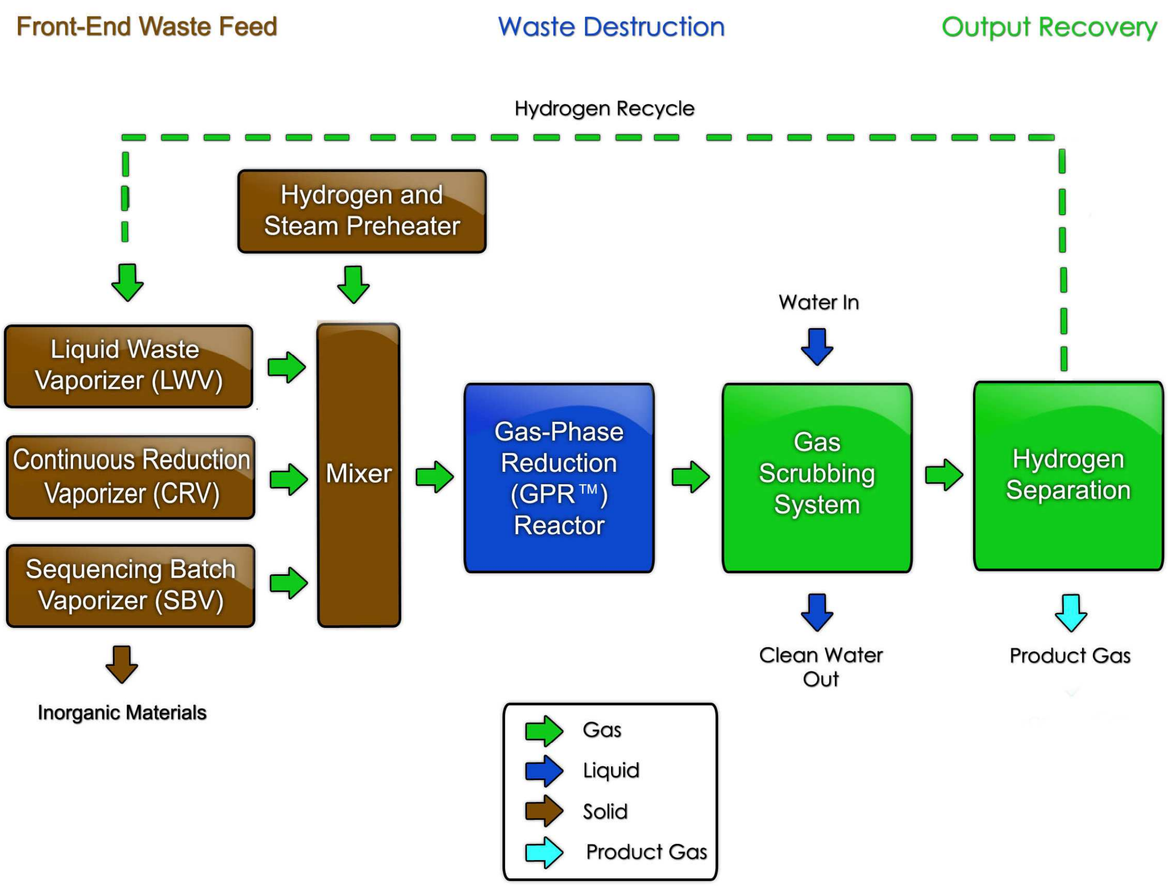
GPCR, GPR, Gas Phase Reduction, Waste to Energy, Non-Incineration, POPs Destruction

GPR TECHNOLOGY BACKGROUND

Gas Phase Reduction (GPR), also known as Gas Phase Chemical reduction (GPCR), is a proven, non-incineration technology for the destruction of hazardous organic chemicals and has been successfully applied to pesticides, dioxins, PCBs, CFCs, and chemical warfare agents. The process involves the heating of organic compounds in a hydrogen atmosphere at temperatures of 850°C to 900°C. Chlorinated hydrocarbons, such as polychlorinated biphenyls (PCBs) are chemically reduced to methane or natural gas and hydrogen chloride (HCl). The HCl is further reduced to sodium chloride (NaCl) in the scrubber. The technology is suitable for organic wastes in all matrices including soil, sediment, sludge, high-strength oils, watery wastes, and bulk solids such as electrical equipment, equipment casings, drums, etc. Many of the outputs from waste treatment are recyclable. Treated electrical equipment for example is suitable for scrap metal recycling, and the product gas output that consists mainly of methane can be used as a fuel for heating, transportation, or electricity generation.

An overall process block flow diagram of the process is given as Figure 1 below. Depending upon the waste matrix, various front end devices may be used. Liquid wastes such as PCB oil are processed in the LWV, land filled wastes or contaminated soils are processed in the CRV, and chemical stockpiles of drummed waste and other bulk solids are processed in the SBV. For all of the front end devices used, the waste organic compounds are vaporized in an atmosphere of hydrogen and steam. Then they are conveyed to the Reactor at 875ºC where destruction by hydrogen occurs. The processed gas consisting mainly of hydrogen, steam, methane, and hydrogen chloride then flows to the scrubber where heat, acid, water, and particulate are removed. The hydrogen chloride in the processed gas is removed by neutralization with sodium hydroxide or lime. The scrubbed processed gas is then compressed and reheated to facilitate hydrogen separation using a membrane technology. The hydrogen rich gas is then recycled back to the process input while the hydrogen lean, methane rich gas, or product gas, is held and tested prior to release as a process fuel.

Figure 1. Process Block Flow Diagram



The GPR technology meets the following key criteria for POPs destruction:

- The technology does not involve combustion in the destruction process. The Process uses hydrogen and high temperature to chemically reduce rather than oxidize the organic waste compounds. The absence of oxygen in the destruction process precludes the formation of dioxins or furans which require oxygen for their formation.
- The technology operates in essentially a closed system. All process effluent streams are contained and analyzed to ensure that no hazardous compounds are released into the environment. If any of the process effluent streams exceed the allowable discharge criteria then the waste streams can be reprocessed prior to release.
- The technology achieves total destruction efficiencies (DEs), for POPs and other substances of concern that approach 100%. Extensive testing of the technology has demonstrated destruction efficiencies that exceed 99.9999% (six nines) for all POPs wastes tested. The destruction efficiency calculation includes all effluent streams as opposed to the DRE which only include gaseous emissions.
- The technology is commercially available for technology transfer. The GPR technology has been used commercially for PCB destruction and cleaning of transformers and electrical capacitors in Kwinana, Western Australia, and in St. Catharines, Ontario, Canada.

PESTICIDE AND RELATED TREATMENT EXPERIENCE

The GPR technology was used for pesticide treatment by Eco Logic Australia in Kwinana beginning in 1995 with treatment of DDT residuals collected by the Western Australia Department of Agriculture. The plant also treated miscellaneous mixed pesticides for the Environmental Protection Agencies (EPAs) of Victoria and South Australia that were stockpiled during collection programs in the 1980s. In late 1999, the Kwinana plant began treating wastes owned by a local pesticide manufacturing client. The pesticides were mainly chlorophenol compounds (2,4-D, 2,4,5-T) but also included bromoxynils, molinate, simazine, terbutryn, diuron, atrazines, etc. The wastes were mixed together, and the mixtures were almost 100 percent organic content.

Hexachlorobenzene (HCB) Trials

In April of 1999, a commercial trial was executed on HCB waste for a former chlor-alkali manufacturer in Australia. The waste treated was a dry crystalline material created as a by-product during the manufacture of chlorinated solvents, containing primarily HCB (84 percent). The waste was stored in polypropylene bags, which were in turn packed into polypropylene-lined drums. The drums were loaded into the SBV for processing. Please refer to figure 2 and figure 3 below. The quantity of waste in each drum ranged from 117 to 254 kg. The test program involved three separate test runs of 3, 9 and 27 drums, processing 514, 1,584 and 4,610 kg of waste, respectively. Only 2% of the input mass was present following treatment. This material was tested and found to be silicon and carbon residue. The HCB was destroyed in the reactor with a DE >99.9999% for all tests.

Figure 2 is a photograph of the SBV used in Kwinana, Western Australia.

Figure 3 is a photograph of the drummed HCB waste placed inside of the SBV in Kwinana

Results

All of the relevant experience gained and proven with the GPR technology is the result of operations by Dr. Hallett's previous company in co-operation with Environment Canada, the Ontario Ministry of the Environment, the Michigan Dept. of Natural Resources, the U.S. Environmental Protection Agency, the Dept. of Environment of Western Australia, and the Dept. of Environment of Australia. Lessons learned include improved operations and materials handling to reduce manpower and increase equipment availability while simultaneously increasing the waste throughput. A new scrubber design with improved pH control is a direct result of the HCB trials. Table 1 below summarizes some of the regulatory testing to date.

Table 1. Summary of Regulatory testing using the GPR Technology.

Project	**Contaminant**	***Destruction and Removal Efficiency (%)***	***Target Criteria (%)***
Bay City (oil – 3 tests) (250 000 ppm PCB in oil)	Tetrachloroethene	> 99.99	99.99
	PCBs	> 99.9999	99.9999
General Motors of Canada Limited (PCB Askarel Oil - 3 tests)	PCBs	99.9999996	99.9999
	PCBs	99.9999985	
	PCBs	99.9999808	
95%PCB Oil (Kwinana Regulatory Testing)	PCBs	99.999998	99.9999
17%DDT in Toluene (Kwinana Regulatory Testing)	DDT	99.999984	99.9999
PCB Oil (Japanese Regulatory Testing)	PCBs	99.99998098	99.9999
	PCBs	99.99999977	99.9999
HCB Treatment Trials (HCB crystals - 3 Tests)	HCB	99.999999	99.9999
	HCB	99.999999	99.9999
	HCB	99.99999	99.9999

NATURAL ENERGY SYSTEMS INC.

Natural Energy Systems Inc. was founded to implement the proprietary Gas Phase Reduction (GPR) process invented by two of the Company's founders, by way of providing 'turnkey' processing plants to customers who will process organic matter and organic waste into a hydrogen enriched methane gas. In February 2009, Dr. Hallett and Mr. McEwen submitted a new patent with the United States Patent Office entitled PROCESS FOR THE CONVERSION OF ORGANIC MATERIAL TO METHANE RICH FUEL GAS. The new patent builds on the technology of the first patent, optimising the conversion of organic wastes to a clean burning Product Gas and expanding the application of the technology to many waste types. The dramatic improvements that are included in the new Patent, relate to lowered operating temperatures, elimination of tar formation which hampers the continuous processing and the use of alternative energy forms, such as Ultra Violet in the chemical process. These coupled with significant hydrogen recovery, have lowered the operating costs of the process by over 50% as compared to the hazardous waste processing plants constructed in the 1990's. For the purposes of the initial launch of the Company, four major applications have been prioritized for development and implementation. These are:

- Municipal Waste (sewage sludge and solid garbage);
- Industrial Waste (tires, PET bottles);
- Hazardous Waste (PCBs, POPs, pesticides, warfare agents); and
- Mineral & Organic Matter (coal, biomass).

Examples of the implementation of the GPR technology include the conversion of Sewage Sludge and Municipal Solid Waste to clean burning Product Gas. This is a non-incineration method of conversion. The improved process has made the cost and environmental effect of processing these wastes commercially feasible, especially where the current sewage disposal methods are to pump the sewage sludge into oceans and rivers. The GPR process does not require any disposal of sewage into the environment and recovers large amounts of potable water that meets or exceeds World Health Organization standards. This water has been found to be as valuable a commodity as the hydrogen-rich natural gas.

A GPR plant treating raw sewage sludge at a rate of 20 dry tonnes per day produces enough Product Gas to generate 540 kW of electricity. This is equivalent to generating $US 35.00 per tonne of waste processed. When the same plant is used to process wastes such as wood or tires, then the energy generated can approach $US100.00 per tonne processed. The NES GPR processing plant is very versatile and this same plant could be used to successfully process sewage waste, municipal solid waste, medical wastes from hospitals, rendering wastes from meat processing, agricultural wastes, and hazardous wastes. The attraction of this option is that by blending small quantities of POPs wastes with other commercial wastes, the effective cost per tonne can be greatly reduced.

We are currently designing and building a demonstration unit that will fit into two ISO sea containers. This unit will be available in 2010 to conduct treatability studies at client sites. Destruction Efficiencies and the quality of the Product Gas will also be demonstrated.

Natural Energy Systems is a 'waste to energy' company. Our mission is to improve the quality of the environment by converting organic material into a clean burning fuel that will provide a lasting and sustainable benefit for mankind.

Section 5: OCPs and other POPs monitoring, modelling, risk assessment

MONITORING OF OBSOLETE PESTICIDES IN AGRICULTURAL SOILS OF THE CZECH REPUBLIC

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Abstract
Obsolete pesticides are substances strongly lipophilic, highly chemical and biological stable, with high ability to bioaccumulation. These all lead to their persistence and world-wide distribution in the environment. Environmental hazard and human health risk are the main reasons for a long-term monitoring of these substances in the soils. In order to determine and evaluate pesticides contents in the soils, the Central Institute for Supervising and Testing in Agriculture (CISTA) carries on “Basal soil monitoring” (BSM) system, supported by the Ministry of Agriculture. Ninety soil samples are collected each year from 40 BSM plots and 5 samples from protected areas for pesticides determination, always from two horizons (topsoil, subsoil). Determinations of four (α–, β–, γ–, δ–) isomers of HCH, HCB and DDT, DDE, DDD (o´,p´and p´,p´isomers) were performed in CISTA labolatory.
Based on our results is clear that HCB and DDT (and metabolites) contents in monitored localities are stable in years. However, contents of HCB and DDT in two sampled horizons are different. These findings were statistically proved by Kruskal-Wallis test. HCH contents are negligible.

Key-words: obsolete pesticides, monitoring, HCB, HCH, DDT

Introduction
A pesticide is any substance or mixture of substances intended for: preventing, destroying, repelling or mitigating any pest. Obsolete pesticides are defined as stocked pesticides that can no longer be used for their original purpose or any other purpose and therefore require disposal. Pesticides can cause harm to humans, animals, or the environment because they are designed to kill or otherwise adversely affect living organisms. Some pesticides are persistent organic pollutants and contribute to soil contamination. This paper is focused on DDT and its metabolites (and its isomers), four isomers of HCH and HCB - typical obsolete pesticides. These pesticides are parts of Stockholm convention, which is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically and accumulate in the fatty tissues of humans and wildlife.
Observation of the obsolete pesticides in agricultural soils is carried out by Central Institute for Supervising and Testing in Agriculture (CISTA) within the frame of programme “Basal soil monitoring” (BSM) from 1998. This programme is supported by the Ministry of Agriculture.

Materials and methods
Pesticides, mentioned above, are monitored at 45 observing plots. The set of observing plots of the BSM system was established in 1992. BSM data are essential for soil quality observing. The BSM is performed by CISTA. Monitoring net consists of 214 monitoring plots; 187 plots belong to basal system, remaining 27 are parts of subsystem of contaminated plots.
The observing plots are defined as rectangles covering an area of 1000m^2 (25 x 40m). Each plot is characterised by terrestrial coordinates, morphology of terrain, climatic and soil conditions. On each observing plot was dug and described a soil pit.

Organic pollutants contents are determined annually in 90 soil samples. The arable soil samples are taken up from the topsoil (0 – 30 cm) and subsoil (30 – 60 cm, in hop gardens from topsoil (10 – 40 cm) and subsoil (40 – 70 cm), on grassland from the horizons (0 – 10 cm, 11 – 25 cm, always after excluding of upper grass layer). Sampling depth in protected areas depends on diagnostic horizons. Samples were immediately put into portable camping fridge and transported to the laboratory. Samples were frozen until chemical analysis.
Determination of pesticides content in the soil samples was performed in accredited analytical laboratories of CISTA. Pesticides has been analysed using Varian GC-MS system with quadrupole analyzer in MS/MS mode.

Results and discussion
As mentioned above 90 soil samples are collected each year. Results of descriptive statistics are shown in Table 1. Results of HCH are not displayed because HCH contents in the BSM soil samples are negligible and most of them do not exceed the limit of quantification (LOQ = 0,5 ppb). LOQ is exceeded in the samples from about 10 monitoring plots, maximal contents are around 4,4 ppb. Data evaluation does not show statistically significant differences neither between horizons nor years. These measurements do not correspond with data from other countries. Average value of 1390 samples from Slovakia was 25 ppb, HCH contents in Katowice (Poland) soil samples ranged from 1,1 to 11 ppb and in Kraków (Poland) soil samples from 0,36 to 110 ppb (Holoubek et al., 2000), range of HCH values in Irish soil samples was 0 – 12,4 ppb (McGrath, 1995), in Romania 1 – 715 ppb (average 35 ppb) (Motelic et al., 2001) and Bailey et al. (1999) mentioned lindan content in Canadian soils in range 1 – 14 ppb.
Table 1 shows descriptive statistics for sum of DDx (sum of o´,p´ and p´,p´ isomers of DDT, DDE, DDD) and DDTtotal (sum of o´,p´ and p´,p´ isomers of DDT + DDE + DDD). Sum of DDT and its metabolites and their proportions on the monitoring plots of BSM were displayed in Figure 1. As expected the contents of DDx in the BSM samples increase in sequence DDD < DDE < DDT. At 70. of the last century typical levels of DDTtotal contamination are considered values around 2000 ppb in arable land and 10 ppb in other soils (Velíšek, 1999). Contrary to this estimation medians of DDTtotal in BSM arable soil samples range from 2,25 to 658 ppb in topsoil (median 22,2 ppb) and 1,50 - 710 ppb in subsoil (median 13,1 ppb). Lower values of DDT content in arable soils are mentioned by McGrath (1995) in Irish arable soils - 0,02 – 89,7 ppb. The same level of contamination is cited for Katowice (Poland) – 23 – 260 ppb and enhanced for Kraków (Poland) – 4,3 – 2400 ppb (Holoubek et al., 2000). Likewise Corona-Cruz et al. (1999) presents in Mexican arable soils - 82,6 ppb (in malarian areas DDT contents could be up to 1000x higher), Motelic et al. (2001) 86 ppb in Romanian arable soils (with maximum 2458 ppb). Andrade et al. (2005) mention DDT content in Argentine arable soils up to nearly 12 000 ppb, actually. Topsoil contents of DDTtotal are higher than subsoil contents with exception of grassland. It could be done by different way of sampling (see Materials and methods).
Medians of HCB in arable soil samples ranged from <0,5 to 52,1 ppb in topsoil (upper layer; median 3,30 ppb) and <0,5 – 19,5 ppb in subsoil (lower layer; median 2,50 ppb). These values coincide with measurement around Kraków (Poland), where range 0,19 – 9,9 ppb of HCB was detected and Katowice (Poland) with range 0,46 – 30 ppb of HCB (Holoubek et al., 2000). HCB contents in the BSM are documented in Figure 2. It is evident that maximal values are in a south-eastern part and in a western part of the Czech Republic. These localities partly correspond with areas contaminated by DDT (Figure DDT). Historically, HCB has been found as an impurity in several chlorinated pesticides (Škrbić et Durišić-Mladenović, 2007).

Conclusions

Evaluation of HCB and DDT contents did not proved statistically significant differencies between years in BSM samples. However, contents of HCB and DDT in two sampled horizons are different. Kruskal-Wallis test proved these differences statistically significant.

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Table 1. Descriptive statistics of organochlorine pesticides in the soil samples of BSMS (ppb)

Plantation	Horizon	HCB				Sum of DDE				Sum of DDD				Sum of DDT				DDT total			
		Aver	Min	Max	Med	Aver	Min	Max	Med	Aver	Min	Max	Med	Aver	Min	Max	Med	Aver	Min	Max	Med
Arable land	Topsoil	4,58	< 0,5	52,1	3,30	25,5	1,25	280	8,54	3,16	0,50	64,1	0,95	29,2	0,50	367	10,5	57,8	2,25	658	22,2
	Subsoil	3,57	< 0,5	19,5	2,50	19,1	0,50	278	4,90	2,53	0,50	58,9	0,50	22,4	0,50	423	7,00	44,0	1,50	710	13,1
Hop garden	Topsoil	8,62	6,60	10,0	8,60	61,9	45,8	93,3	58,1	5,96	3,26	11,7	4,56	147	110	218	131	215	179	316	182
	Subsoil	7,05	2,16	18,4	3,10	27,5	5,59	59,0	17,4	2,85	0,50	5,1	2,80	70,6	15,0	134	44,0	101	21,1	185	64,1
Grassland	Upper layer	6,77	0,50	27,3	4,48	37,3	1,25	180	6,41	4,97	0,50	28,5	0,50	53,2	1,05	256	7,90	95,4	2,80	462	12,3
	Lower layer	6,26	< 0,5	30,8	3,00	34,2	0,95	195	7,07	4,14	0,50	30,4	0,50	62,0	0,95	494	7,68	100	2,50	664	13,9
Protected areas	Upper layer	1,15	< 0,5	5,3	0,60	5,54	0,50	25,4	1,62	1,02	0,50	7,0	0,50	11,5	0,50	82,5	1,57	18,0	1,50	110	3,57
	Lower layer	0,57	< 0,5	2,0	< 0,5	1,41	0,50	8,4	1,05	0,50	0,50	0,5	0,50	1,72	0,50	14,8	0,50	3,63	1,50	23,7	2,20

Figure 1. Sum of DDT and its metabolites and their proportion on the monitoring plots of BSM (medians of contents; ppb)

Figure 2. Content of HCB on the monitoring plots of BSM (medians of content; ppb)

MONITORING OF CONTAMINATIONS OF FOOD, ENVIRONMENTAL MEDIA AND BREAST MILK WITH OBSOLETE PESTICIDES IN BELARUS

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Abstract
Organochlorine pesticides (OCP) were used in Belarus for food stuff production until 1980. Although use of OCP was prohibited in 1979, until recently contamination of food, water, soil, ambient air with obsolete pesticides is still detected. Breast milk from 984 women was collected around the country in rural areas and cities in 2007-2008 in order to investigate the results of environmental protection measures and to ground the monitoring programme.
Frequency of detection of organochlorine pesticides in breast milk in different regions in Belarus varied widely. More frequently β-hexachlorcyclohexane (β-HccH), hexachlorebenzene (HCB) and DDE were detected. None of the samples was free of contamination of OCP. The highest concentration of β-HccH was found in samples of women living in Minsk-city and Grodno region (80,47±5,35 and 80,04±8,38 μg/kg of fat respectively). In Brest and Grodno regions DDT and its metabolites concentration was practically twice as high as in other ones (58,09±9,68 and 63,81±13,32μg/kg of fat respective). Meaningful positive correlation between age of women and concentration of DDE, HCB, sum of DDT and metabolites and sum of HccH and isomers was revealed. No correlation was observed between contaminations of breast milk and results of monitoring of OCP in food and drinking water contamination. Strong connection of concentration of DDT and HCB in breast milk and air pollution by these pesticides detected by passibe sampling analysis was determined. Further investigations are needed to be conducted to confirm that findings. It was found that weight of newborns delivered by mothers with higher concentration of sum of DDT metabolites and HccH isomers and DDE was lower that other newborn infants.

Key words: breast milk, organochlorine pesticides, contamination

Introduction

Organochlorine pesticides were used in Belarus for food stuff production until 1980. Although use of organichlirine pesticides was prohibited in 1979, until recently contamination of food, food stuffs, water, soil, ambient air with obsolete pesticides is still detected. That leads to contamination of breast milk and can pose risks to health of newborns. To access risks to human health, to evaluate environmental contamination, to identify sources of pesticides for humans and to ground risk reduction measures, human biomonitoring in Belarus is conducted since 1998 /1, 2/. High level of breast milk contamination is detected in many other countries and there different opinion about what level of concentration impact health /3, 4, 5/.
The main aim of current study is to evaluate contamination by organochlorine pesticides (OCP) in breast milk, food, drinking water and ambient air contamination in different regions of the republic in order to investigate the results of environmental protection measures, to ground the monitoring programme and prognosticate risks for newborns.

Material and method

Breast milk from 984 women was collected around the country in rural areas and cities in 2007-2008, on the fifth day after childbirth and during the stay of the women in hospital under control of the physician. The investigation took place in every region of the country 103 women in Brest region, 101 – Vitebsk, 84 – Gomel, 150 – Grodno, 98 – Minsk, 101 – Mogilev and 347 in Minsk city. The questionnaire which women were asked to answer was worked out based on WHO recommendation for POPs contamination investigations and included questions concerning physical characteristics (age, height and weight), occupation, place and duration of living, smoking, food prevalence (meat, milk, vegetables, eggs, seafood) and sources of food (grocery store, market, private farm). Separate questions were worked out for medical workers to evaluate the health condition of newborns. Concentration of α-, β-, γ- hexachlorcyclohexane (HccH), heptachlor (HCl) , DDE, DDD, DDT, hexachlorebenzene (HCB) were determined by gas chromatography. Contamination of food and water was evaluated by using existing monitoring data for the period 2002-2007 and ambient air concentration was detected by passive sampling method developed by of Dr. I. Holoubek and his colleagues from Masarik University and conducted in Belarus with RECETOX technical and financial support (Brno, Czech Republic) /6/.

Breast milk contamination

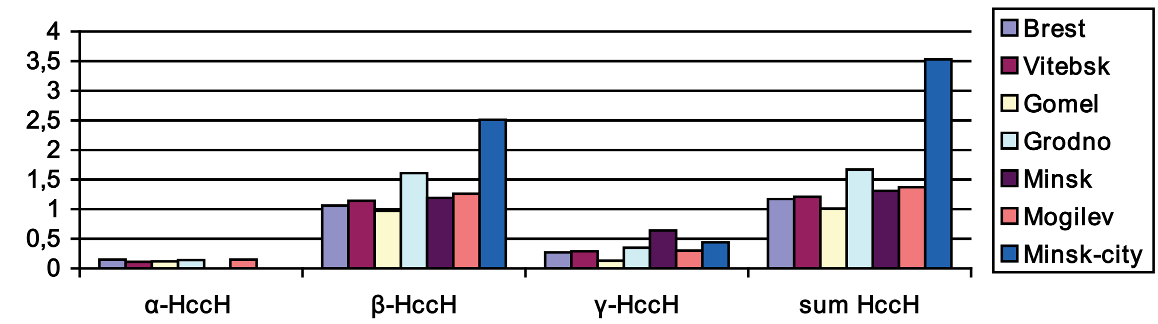
α-HccH was detected in 76 samples that is 7,7% of total amount of milk samples, β-HccH – 829 (84,2%), γ-HccH – 190 (19,3%), HCB – 860 (87,3%), DDT – 503 (51,1%), DDE – 891 (91,5%), DDD – 93 (9,4%), aldrin – 35 (3,5%), HCl – 64 (6,5%). Thus most samples were contaminated with DDT, DDE, β-HccH isomer and HCB. This can be explained by the fact that DDT, HccH and HCB were most widely distributed pesticides in Belarus and used in big amount. α- HccH was not detected above limit of detection in breast milk of women living in Minsk region and Minsk city, and DDD – in Minsk region. All other substances were determined with different frequencies concerning the regions (table 1).

Table 1 – Frequency of detection of organochlorine pesticides in breast milk in different regions in Belarus

Region	N	Organochlorine pestucudes									
		α-HccH N (%)	β-HccH N (%)	γ-HccH N (%)	Sum HccH N (%)	HCB N(%)	DDT N (%)	DDE N (%)	DDD N (%)	Sum DDT N (%)	HCl N(%)
Brest	103	30 (29,1)	92 (89,3)	36 (35,4)	96 (93,2)	101 (98,0)	72 (69,9)	100 (97,1)	15 (14,5)	100 (97,1)	47 (45,6)
Vitebsk	101	11 (10,9)	89 (88,1)	17 (16,8)	89 (88,1)	82 (81,2)	25 (24,7)	88 (87,1)	21 (20,8)	89 (88,1)	3 (2,9)
Gomel	84	4 (4,8)	42 (50,0)	9 (10,7)	42 (50,0)	44 (52,4)	21 (25,0)	44 (52,4)	2 (2,4)	44 (52,4)	8 (9,5)
Grodno	150	20 (13,3)	130 (86,7)	39 (26,0)	135 (90,0)	140 (93,3)	87 (58,0)	145 (96,7)	22 (14,7)	143 (95,3)	38 (25,3)
Minsk	98	0 (0)	76 (77,5)	22 (22,4)	80 (81,6)	83 (84,7)	51 (52,0)	83 (84,7)	0 (0)	83 (84,7)	46 (46,9)
Mogilev	101	11 (10,9)	87 (86,1)	34 (33,7)	89 (88,1)	95 (94,1)	43 (42,6)	94 (93,1)	9 (8,9)	94 (93,1)	15 (14,8)
Minsk city	347	0 (0)	313 (90.2)	33 (9,5)	334 (96,3)	315 (90,8)	204 (58,8)	337 (97,1)	24 (6,9)	336 (96,8)	1 (0,3)
Whole country	984	76 (7,7)	829 (84,2)	190 (19,3)	865 (87,9)	860 (87,4)	503 (51,1)	891 (90,5)	93 (9,4)	887 (90,1)	158 (16,1)

Determined level of concentrations of OCP in breast milk are presented in table 2. None of the samples was free of contamination of at least one of OCP. Concentrations of OCP in breast milk varied in depending on the region and at individual level (fig.1).

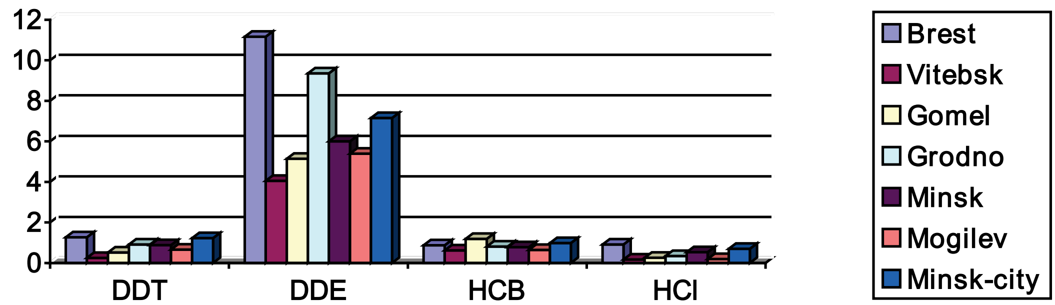
Fig. 1 Contamination of Breast milk with HCCH in regions in Belarus



The highest concentration of β-HccH was found in samples of women living in Minsk-city and Grodno region. But the concentration of γ-HccH was higher in Minsk region and Minsk-city that in other ones. The results show that the concentration of HccH isomers, compared to the data in previous studies (1998, 2003) became lower which can be explained as a result of degradation of pesticides in environmental media and measures that were taken to reduce the risks (prohibition of use, repackaging, safe storage).

Similarly notable variations between regions and cities were determined for DDT and its metabolites residues and also for HCB and HCl ones. Contamination of DDT varied from 0,1 to 6,6 µg/l, DDE – 2,0-58,0 µg/l and DDD – 0,1-2,1 µg/l in different regions. The fact that concentration of pesticides in breast milk of women in cities is similar and even higher than in rural areas can be explained by the differences in sources of food: mostly local in rural areas and from different sources including big part of imported products in cities. In Brest DDT and its metabolites concentration was practically twice as high as in other regions (Fig.2). The results of study indicate that the main metabolite is DDE which is a result of DDT degradation. Rather many samples contain DDT whereas a rather high concentration of DDT is a warning signal especially taking into account that the number of samples that contained DDT were lower in a previous study (2002-2004).

Fig. 2 Contamination of Breast milk with DDT and its metabolites in regions of Belarus



The difference between for HCB and HCl was not so clear. But nevertheless it should be noted that HCl rate is significantly higher in Breast than in Grodno, Minsk and Mogilev regions.

Table 2 – Contamination of breast milk in regions of Belarus with HccH isomers, DDT and metabolites, HCB and HCl.

Region	α-HccH μg/l μg/kg	β-HccH μg/l μg/kg	γ-HccH μg/l μg/kg	Σ HccH isomers μg/l μg/kg	DDT μg/l μg/kg	DDE μg/l μg/kg	DDD μg/l μg/kg	Σ DDT metabolites μg/l μg/kg	HCB μg/l μg/kg	HCl μg/l μg/kg
Brest	0,15±0,02	1,06±0,13	0,27±0,04	1,18±0,13	1,27±0,11	11,16±0,90	0,38±0,10	11,48±0,77	0,87±0,12	0,92±0,16
	5,50±0,80	38,76±4,51	11,30±2,43	42,87±4,79	58,09±9,68	402,73±30,33	13,33±3,61	465,72±43,75	31,23±4,66	38,21±9,74
Vitebsk	0,11±0,01	1,14±0,16	0,29±0,07	1,21±0,16	0,25±0,06	4,06±0,52	0,24±0,04	4,14±0,53	0,62±0,06	0,16±0,07
	4,01±0,51	41,17±6,38	13,59±5,91	43,83±6,46	9,47±2,53	158,07±19,89	7,80±1,58	160,60±20,16	24,25±2,96	8,45±0,12
Gomel	0,12±0,02	0,97±0,17	0,13±0,02	1,01±0,17	0,52±0,08	5,14±0,57	0,20±0,10	5,40±0,60	1,19±0,21	0,26±0,06
	5,80±1,12	34,21±4,76	7,23±1,22	36,31±4,79	21,10±3,69	201,72±24,57	6,83±1,28	212,10±26,15	43,52±7,14	14,07±4,53
Grodno	0,14±0,02	1,61±0,14	0,36±0,07	1,67±0,14	0,91±0,10	9,35±0,89	0,28±0,04	9,50±0,84	0,62±0,06	0,34±0,04
	6,38±1,05	80,04±8,38	17,88±3,79	83,04±8,27	63,81±13,32	450,36±47,34	16,53±3,77	492,18±52,06	42,30±5,25	27,45±9,69
Minsk	-	1,19±0,13	0,64±0,14	1,31±0,14	0,89±0,08	6,00±0,53	-	6,54±0,55	0,78±0,07	0,53±0,08
	-	42,68±3,92	22,98±5,47	46,87±4,17	31,16±2,91	212,58±55,00	-	231,72±17,14	28,31±2,22	21,00±3,47
Mogi-lev	0,15±0,03	1,96±0,16	0,30±0,06	1,37±0,16	0,66±0,11	5,39±0,67	0,38±0,10	5,73±0,68	0,64±0,08	0,19±0,03
	5,59±1,16	54,85±11,75	10,24±1,96	57,97±11,47	22,84±4,06	189,59±7,69	14,34±3,72	201,42±26,14	22,00±2,26	6,23±0,97
Minsk-city	-	2,51±0,15	0,44±0,07	3,53±0,22	1,23±0,07	7,15±0,41	0,80±0,11	7,80±0,42	0,98±0,08	0,70±0,001
	-	80,47±5,35	21,02±5,89	81,88±5,35	39,10±3,21	239,16±12,50	31,21±4,98	264,46±17,14	33,67±3,20	31,82±0,01
Count-ry	0,14±0,01	1,73±0,07	0,36±0,03	2,22±0,10	1,02±0,04	7,26±0,26	0,43±0,04	7,66±0,26	0,86±0,04	0,55±0,06
	5,58±0,47	63,61±2,96	15,70±1,69	65,90±2,94	48,88±3,12	274,84±11,55	17,67±1,97	302,04±12,98	32,70±1,68	25,99±3,97

Correlation between breast milk contamination by OCP and physical characteristics and food preference of women

No correlation with women's weight was revealed. But there was a meaningful positive correlation between age of women and concentration of DDE, HCB, sum of DDT and metabolites and sum of HccH and isomers. That finding corresponds to the data of many other reports.

Women who eat more fish and seafood have higher concentration β-, γ-HccH, HCB and sum of DDT and metabolites. Concentration of all DDT metabolites, HccH and DDE was higher in women that eat eggs more often.

Concentration of OCP in food, drinking water and environmental media

Monitoring of food and drinking water contamination has been performed in Belarus since 1965. During that period the concentration of OCP in all media decreased dramatically and now practically there is no samples that have detectable concentration of OPC. For examples, according to the results of breast milk contamination by DDT study there is meaningful difference between Breast and Mogilev regions. But there is no any difference in food and drinking water contaminations. There is no correlation between contaminations of brest milk and results of monitoring of OCP in food and drinking water contamination.

Strong connection between breast milk contamination and air pollution detected by passive sampling method was detected. For example highest concentration of DDT was revealed in breast milk of women living in Brest region and Minsk city. The same situation was observed in passive sampling air analysis. Similar findings are for HCB. Further investigation needs to be conducted to confirm correlation between breast milk contamination and pollution of air determined by passive sampling analysis method. The very preliminary explanation could be that air pollution samples provide possibility to characterize soil pollution qualitatively and also transboundary transmission.

Influence on newborn infants

It was found that weight of newborns delivered by mothers with higher concentration of sum of DDT metabolites and HccH isomers and DDE was lower that other newborn infants.

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CONTENTS OF ORGANOCHLORINATED PESTICIDES AND POLYCHLORINATED BIPHENYLS IN SOIL AND SEDIMENTS IN REPUBLIC OF MOLDOVA

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Abstract: Contamination of soil is a 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.

Keywords: Polychlorinated biphenyls (PCBs), organochlorinated pesticides (OCPs), Maximum Allowable Concentration (MAC), State Hydrometeorological service (HSH), Republic of Moldova (RM), Persistent Organic Pollutants (POPs).

Introduction

Article 1 of the Stockholm Convention on Persistent Organic Pollutants requires Parties 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). Fourth meeting of the Conference of the Parties included a nine new POPs in Annex A, B, C.

The Republic of Moldova ratified the Stockholm Convention on Persistent Organic Pollutants by the Law no. 40-XV from 19.02.2004 on ratification of the Stockholm Convention on POPs (Monitorul Oficial, 2004, no. 39-41).

1. 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. Large quantities of pesticides, including POPs, were used 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). The peak of pesticides use was registered in 1975-1985, but has reduced dramatically over the last 10-15 years (from 38,300 tons in 1984 to some 2,800 tons in year 2000 as active ingredient).

The absence in the past of controls on pesticides imports, storage and use have resulted in the stockpiling of banned and useless pesticides, 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 tons of DDT. Also 1,700 tons of pesticides were stored in 344 warehouses in country site.

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.

More than 2200 tons of toxic materials were shipped in 2006-2008 to France and disposed of. In energy sector, 18660 obsolete power capacitors containing polychlorinated biphenyls (PCB) have been dismantled and eliminated from high voltage transformer substations. The total weight of such wastes reaches 934 tons. 1292 tons of pesticides from agricultural sector have been eliminated from 13 centralized warehouses . About 2000 tons of pesticides from the other district warehouses should be eliminated in the near future. The Ministry of Ecology and Natural Resources has launched, under the ongoing projects, the national inventory of PCB contaminated dielectric oil, of POP contaminated sites and pilot activities for remediation of sites contaminated with POP pesticides.

2. POPs Monitoring in the Republic of Moldova

2.1. OCPs contents in soil

According to the State Hydrometeorological Service Monitoring Program the determination of OCPs such as DDTs and HCHs are performed in soil from agricultural areas during 30 years. Pesticides from stockpiles with obsolete pesticides and transformer oil from 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 dumps and soil around the electric power installations and sediments from main water bodies of RM was included in Monitoring Program of State Hydrometeorological Service later in years 2003-2005.

Organochlorinated pesticides DDTs and HCHs have been widely used in the 60-70th 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 as 0.1mg/kg. The application of DDT was banned in year 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 received during the years 2006-2008 shows that contents of DDTs are not high and mean concentrations don’t exceed norm, the mean contents of DDTs varies from 0.004 to 0.083 mg/kg (Figure 1).

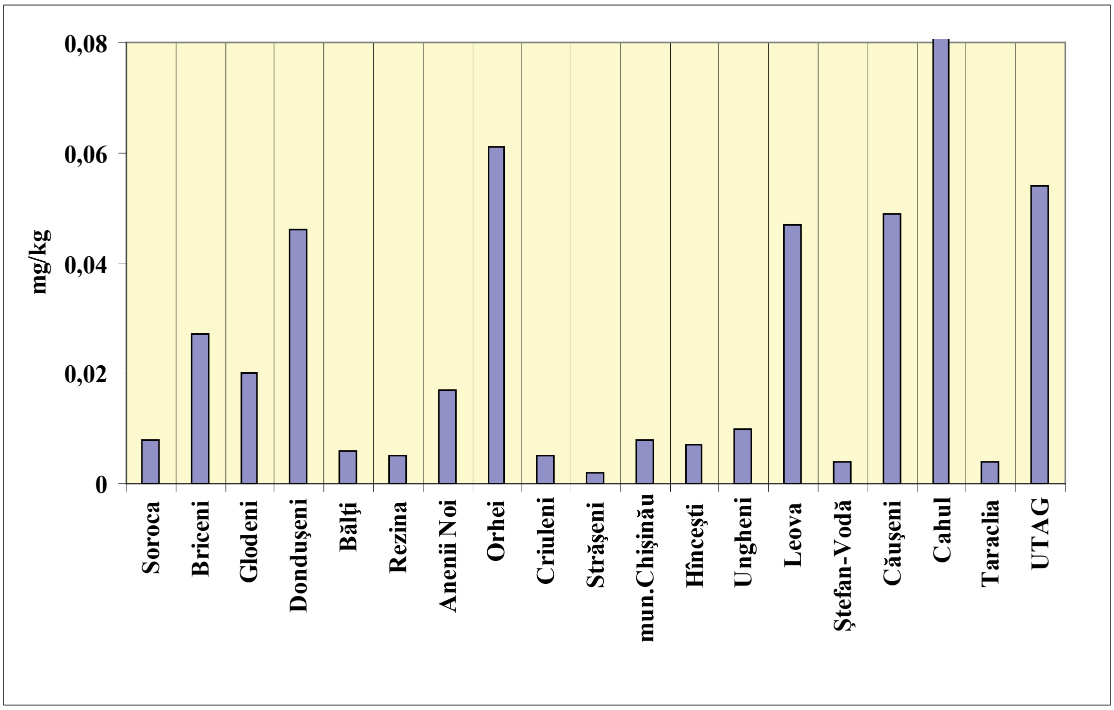

Figure 1. Mean contents of DDTs in agricultural soils of Republic of Moldova in 2006-2008 years

During last three years were investigated 23146 ha of agricultural areas - 21263 ha are not polluted and 1883 ha are polluted with maxima 0,905 mg/kg (Figure 2).

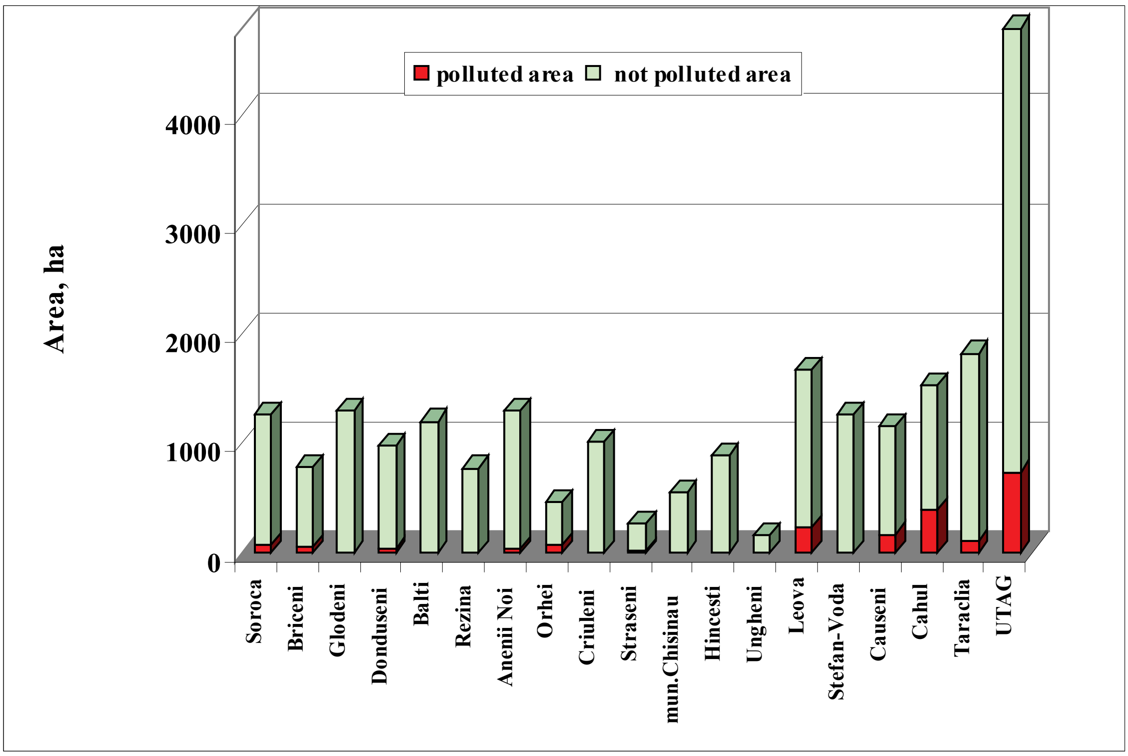

Figure 2. Volume of polluted area against to total volume of investigated area

Soil around the 28 warehouses was investigated during the last six years. Soil around the nine warehouses is not polluted with DDTs - the contents of DDTs in soil didn't exceed norm of quality value and varied from 0,033mg/kg to 0,081 mg/kg, in soil around eleven warehouses were revealed exceeding of norm of quality value of DDTs from 2,2 MAC to 16,2 MAC. Soil around of eight warehouses is polluted at the high and extreme high level and varied from 30,9 MAC to 1812,2 MAC (Figure 3 and 4).

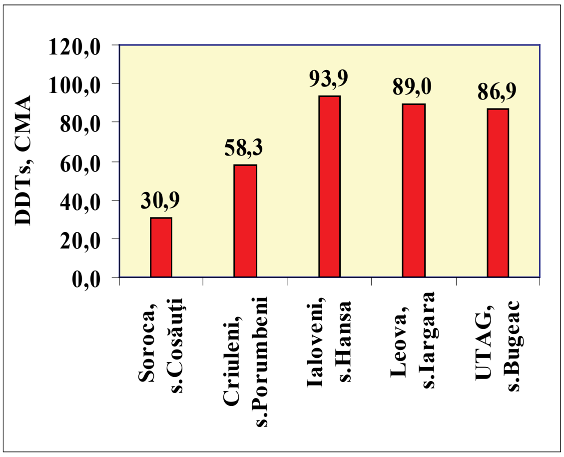

Figure 3. Contents of DDTs in soil around the warehouses at the high level

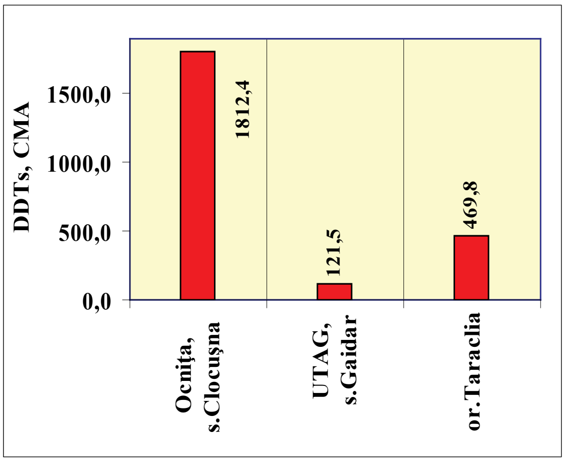

Figure 4. Contents of DDTs in soil around the warehouses at the extreme high

Contents of HCHs in agricultural soils in selected districts during four last years are not high, maximum concentration is 0,029 mg/kg (0,29 MAC). Soil around the nine warehouses is not polluted with HCHs, the contents of HCHs in soil didn't exceed norm of quality value and varied from 0,001 mg/kg to 0,043 mg/kg, in soil around fifteen warehouses were revealed exceeding of norm of quality value of HCHs from 1,3 MAC to 18,0 MAC. Soil around the four warehouses is polluted at the high and extreme high level and varied from 26,4 MAC to 116,34 MAC (Figure 5).

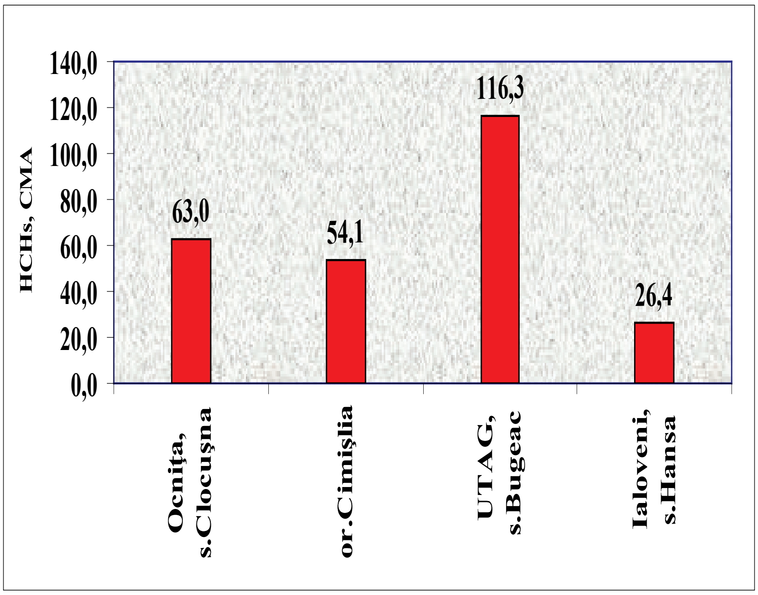

Figure 5. Contents of HCHs in soil around the warehouses at the high and extreme high level

2.2. PCBs contents in soil in around the energy substations

The norm of PCBs in soil (MAC) is 0.06 mg/kg. Contents of PCBs in agricultural soils in selected districts during four last years are insignificant and didn't exceed maximum allowable concentration, maximum concentration is 0,044 mg/kg (0,73 MAC). During the 2005-2008 years sixteen substations were investigated. The PCBs contents were determined in soil in depth 0-10 cm around the PCB-containing capacitors in the electrical substations that are in conditions of leakages due to corrosion. The results show exceeding norm of PCBs in soil in 13 electrical substations from 16 investigated (Table 1).

Data received shows that soil investigated from 10 substation is polluted at the high and extreme high level, contents of PCBs in soil, varied from 1,23 mg/kg to 4317,95 mg/kg, in 3 substations soil are polluted, contents varied from 0,08 mg/kg to 0,75 mg/kg, and in 3 substations soil is not polluted with PCBs.

Table 1. *Contents of PCBs in soil in electrical substations*

Location of Substation	**Max. value**	**Max. value**		**Location of Substation**	**Max. value**	**Max. value**
	mg/kg	**MAC**			**mg/kg**	**MAC**
Vulcăneşti	4317,95	71965,8		Soroca	1,97	32,8
Briceni	1770,51	29508,6		Edineţ	1,23	20,5
Orhei	1016,13	16935,5		Drochia	0,75	12,5
Donduşeni	76,98	1283,1		Străşeni	0,57	9,5
Comrat	50,49	841,6		Străşeni	0,08	1,4
Ungheni	38,96	649,3		Costeşti	0,03	0,5
Ceadîr-Lunga	6,18	103,1		Leova	0,05	0,8
Lipcani	2,69	44,9		Hînceşti	0,01	0,1

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 includes 14 sampling sites established in main water bodies of Republic of Moldova. As a result the most samples contained organic compounds. DDTs concentrations vary from 0,4 to 10,9 mkg/kg, HCHs concentration - from 0,1 to 0,7 mkg/kg, PCBs contents vary from 0,5 to 14,1 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.

CONCLUSIONS

- Contents of DDTs and HCHs in agricultural soil are not high and 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

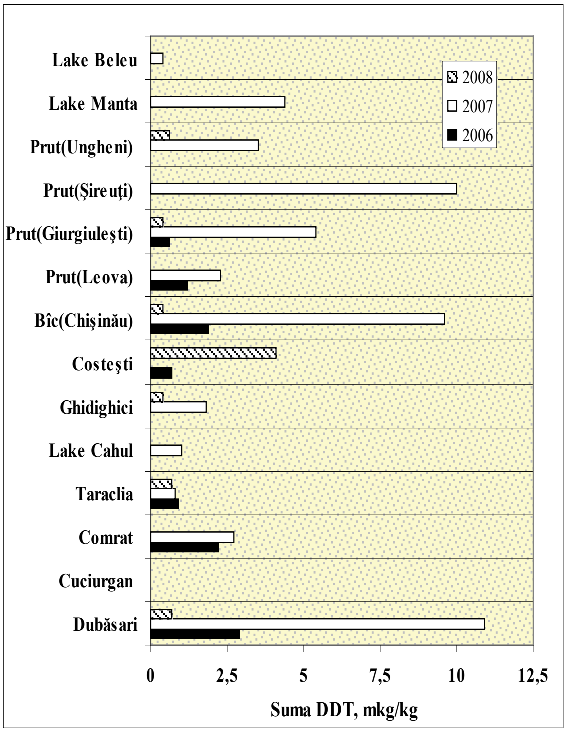

Figure 6. DDDs contents in sediments

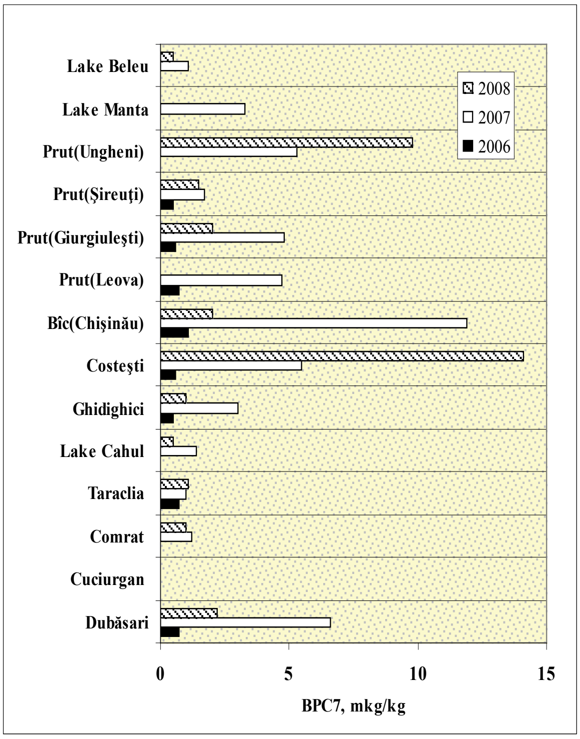

Figure 7. PCBs contents in sediments

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ORGANOCHLORINE PESTICIDES RESIDUE IN LAKES OF KHOREZM, UZBEKISTAN

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Abstract
The Khorezm province in northwest Uzbekistan is a productive agricultural area within the Aral Sea Basin that produces cotton, rice and wheat. Various organochlorine pesticides were widely used for cotton production before Uzbekistan's independence in 1991. In Khorezm, small lakes have formed in natural depressions that receive inputs mostly from agricultural runoff. Samples from lake waters and sediments, as well as water from the Amu Darya River (which is the source of most of the lake water) have been analyzed to study variations in the concentrations of organochlorine pesticides residues during the year. Low concentrations of DDT, DDD, DDE, α-HCH and γ-HCH compounds were found in water and sediment samples. The concentration of persistent organochlorine pesticides (DDT and HCH) in water and sediment is much lower than the maximum permissible concentrations that exist for water and soil. According to these preliminary results, the investigated lakes in Khorezm appear to be suitable for recreation or for aquaculture.

Key words: organochlorine pesticides; DDT; HCH; water; bottom sediment; lakes; Khorezm province; Uzbekistan

Introduction

The Khorezm province is a productive agricultural area within the Aral Sea Basin. Cotton, rice and wheat are the major commercial crops in this province. Before Uzbekistan's independence in 1991, various pesticides were used for the production of cotton and other crops [1] in greater qualities than at present. Among those pesticides, persistent organic pollutants such as the organochlorine pesticides - DDT and HCH were used in large quantities. According to the Uzbekistan State Register of Chemical and Biological Plant Protection Reagents more than 180 substances (i.e. pesticides, herbicides, fungicides, etc.) are presently allowed to be used in agriculture [2]. However, DDT and HCH have been placed on the register of banned and restricted active and non-active ingredients of plant protection agents [3]. Application of DDT and HCH has been prohibited since 1983 and 1991, respectively. Despite the bans, organochlorine pesticide residues have been observed in the environment (soil, surface and groundwater, bottom sediments, biota) [4].

There are more than 450 small lakes in Khorezm province. Many of these lakes have formed from irrigation runoff and diversion of water from agricultural fields and are potentially important receptors of the pesticide and fertilizer residues used in agriculture.

The objectives of the present Khorezm-province study are to (1) investigate the occurrence and distribution of organochlorine pesticides residue in lake water, sediment and river water samples and, (2) determine if the lakes are suitable for recreation or commercial activities.

Sampling

Water and bottom sediment were collected for the determination of DDT and associated metabolites (DDE and DDD), and α-HCH and γ-HCH isomers in 13 lakes and the Amu Darya River in Khorezm (Fig. 1). Water samples were collected at approximately monthly intervals from August 2006 to June 2007 using sampling protocols developed in Uzbekistan [5] and internationally. Bottom sediment samples were collected from near the center of the lakes in 2007 using a Ponar grab sampler. All field samples were stored in a freezer, transported to the Hydrometeorological Research Institute laboratory and kept in a refrigerator until analyzed.

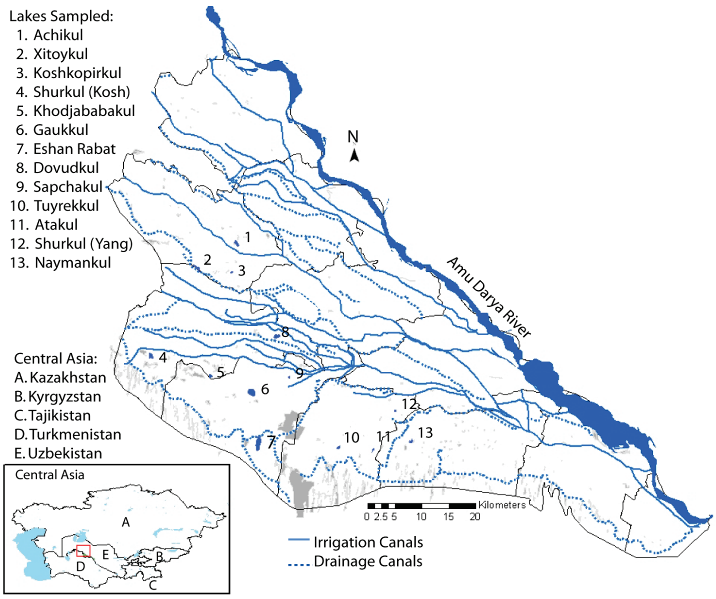

Fig. 1. Studied lakes in Khorezm, which is located in the northwest of Uzbekistan. Grey shaded areas are lakes

Analytical methods

The methodology used to analyze pesticide residues in waters and sediments followed the standard techniques used by Uzhydromet [6,7]. Organochlorine pesticides were analyzed by gas chromatography with an electron capture detector.

Water

The water samples were processed using the following procedures: filtration with Whatmann glass fiber filters (0.45 μm); double extraction of pesticides with *n*-hexane + shaking; extract cleanup, using concentrated sulfuric acid for elimination of organic substances; drying of extract with Na_2SO_4; reconcentration of the extract; and injection of the extract into the chromatograph.

Sediment

The analytical procedure for the sediment samples was: homogenization of wet sample; air drying at 20^{o}C; double extraction of pesticides with *n*-hexane and acetone; extract cleanup, using concentrated sulfuric acid for elimination of organic substances; drying of extract with Na_2SO_4; reconcentration of the extract; and injection of the extract into the chromatograph. In addition, the absolute dried weight of the sediment was determined by weighing homogenized and air-dried samples after they were heated in a muffle furnace at 105^{o}C for 6 hrs. Samples were checked to ensure they were at a constant weight to ensure they were dry.

Results and discussion

Concentrations of DDT and its associated metabolites in lake water were from below detection (BD; detection limit for all pesticides is approximately 0.005 μg/L) to 0.10 μg/L. Concentration of α-HCH in lake and river water were between BD to 0.02 μg/L, and γ-HCH was between BD to 0.027 μg/L. The highest concentrations of the investigated pesticides in water were observed in Tuyrekkul Lake in June 2007. Fig. 2 shows the seasonal variation of organochlorine pesticides in water of selected lakes and the Amu Darya River from August 2006 to June 2007. Concentrations of both HCH and DDT appear to increase marginally during the summer growing season (March – June samples), however, concentrations are near the detection limit of the methods and these apparent increases are mostly within the uncertainty of the analyses.

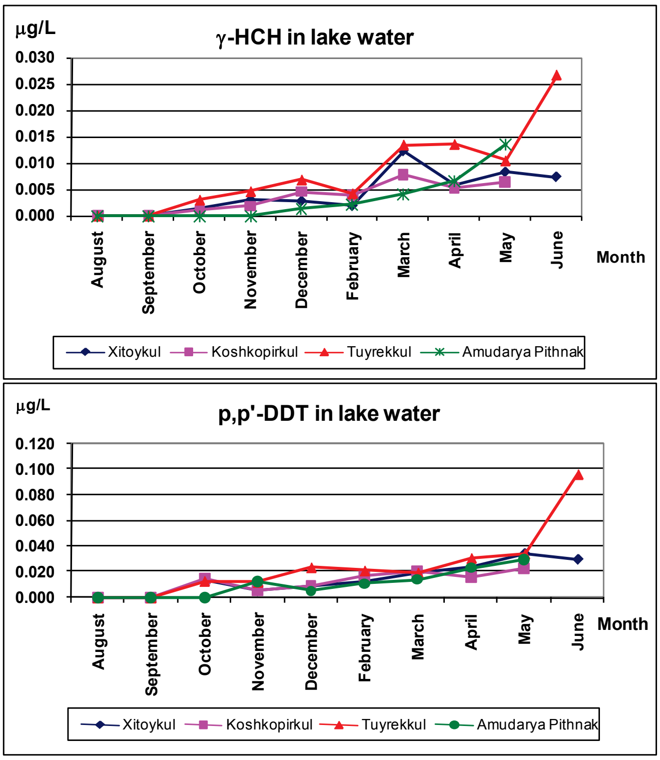

Fig. 2. Temporal variations of □-HCH and p,p'-DDT in selected lakes sampled in this study and the Amu Darya River

Fig. 3 shows the mean concentration of organochlorine pesticides in water of selected lakes and the Amu Darya River over the sampling period. The observed concentration of organochlorine pesticides was lower than Maximum Acceptable Concentration (MAC) for those pesticides for water (MAC in water are 0.1 mg/L for DDT and 0.002 mg/L for HCH) [7,8].

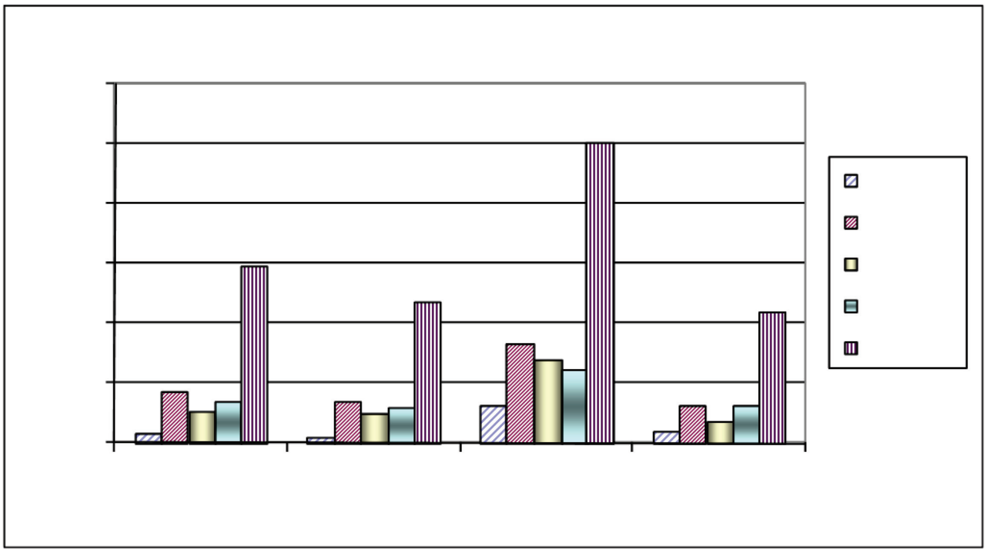

Fig. 3. Mean organochlorine pesticide concentrations in selected lakes and the Amu Darya River

Lake bottom sediments may be the focal point for the accumulation of contaminants entering from the surrounding catchment, in particular pesticides that may be bound to sediment, such as organochlorine pesticides. In some cases, the bottom sediments can be a secondary source of water contamination. Therefore, the investigation of contaminant concentrations in bottom sediments is an important part of assessing the ecological condition of lakes. Concentrations of DDT and associated metabolites in lake bottom sediments were from BD (BD for all pesticides is approximately 0.001 mg/kg) to 0.011 mg/kg. For α-HCH concentrations ranged from BD – 0.002 mg/kg and for γ-HCH concentrations ranged from BD – 0.003 mg/kg, with the highest observed concentration of DDD and both isomers of HCH at Atakul Lake (Fig. 4). The land use surrounding Atakul is 93 percent agricultural.

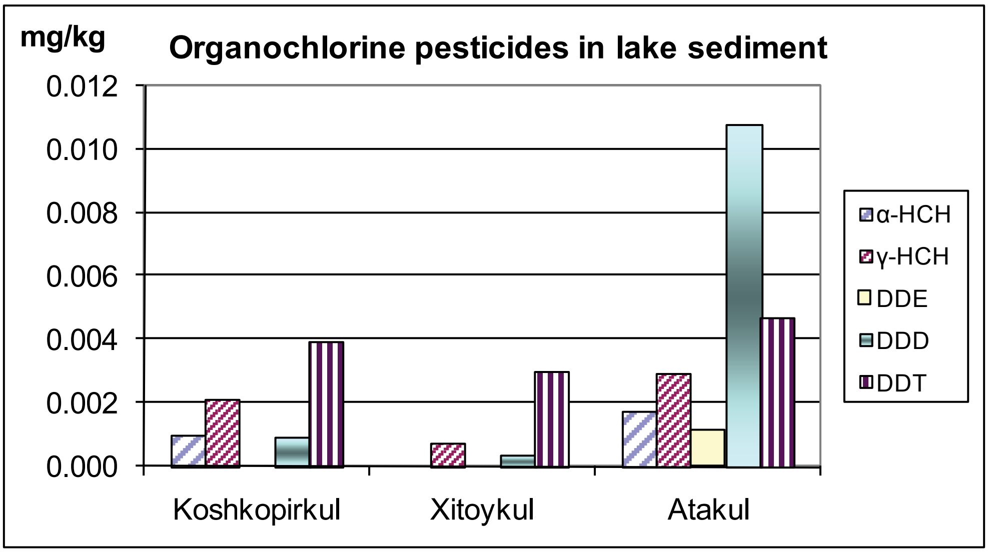

Fig. 4. Organochlorine pesticide concentrations in selected lake samples

The MAC level for pesticides in bottom sediments has not yet been established in Uzbekistan. Therefore, it is practical to compare the observed concentration of pesticides in lake sediments to MACs established for soil. The results indicate that organochlorine pesticide concentrations in lake sediments were lower than the MAC in soil (MAC in soil are 0.1 mg/kg for DDT and 0.1 mg/kg for HCH) [8,9].

Conclusion

The results of the research show that the concentration of persistent organochlorine pesticides (DDT and associated metabolites and HCH isomers) in water and sediment is much lower than the MACs that exist for water and soil. Although no MAC is available for bottom sediment in Uzbekistan, according to these preliminary results, the investigated lakes in Khorezm appear to be suitable for recreation or for aquaculture.

Acknowledgements
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RESIDUAL AMOUNTS OF CERTAIN PERSISTENT ORGANIC POLLUTANTS IN ENVIRONMENTAL MEDIA, FOODSTUFFS AND BIOMEDIA OF THE REPUBLIC OF ARMENIA

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Abstract

The organochlorine pesticides (OPs) such as HCH, DDT should be first of all related to persistent organic pollutants (POPs) likewise polychlorinated biphenyls (PCBs). The environmental load of mentioned hazardous chemicals is a result of OPs and PCBs intentional production and application, as well as unintentional production.
From the point of view of ecology and hygiene the substantial matrices for HCH, DDT and PCBs accumulation are soil, water, bottom sediments, hydrobionts, and foodstuffs, especially those with high fat content. Therefore, we studied samples of:

- water of lakes (Sevan), rivers, and drainage system;
- biomedia from Sevan Lake: periphyton, macrophytes, fish tissues, crawfish tissues;
- bottom sediments from the lake, rivers, waste water drainage system;
- soil from the vicinity of energy providing facilities, sites of waste-dumps and former pesticide storehouses;
- foodstuffs: meat, cheese, milk, and eggs.

The aim of research was to study levels of POPs pollution in environmental media and foodstuffs.
Mentioned POPs were determined using the method of gas-liquid chromatography.
Data obtained upon analyses for HCH, DDT and PCBs signify that:

1. Concentrations in environmental media are at levels which do not exclude their migration from the environment to foodstuffs and living organisms;
2. The problem of pollution by organochlorine compounds is mainly connected with PCBs (100 % positive samples) and not with the OPs;
3. Highest level of soils, bottom sediments and water pollution by PCBs was revealed near facilities of the energy complex (HPPs, TPPs, transformer stations, etc.), waste dumps, at which the exceedance of hygienic standards was observed in most cases;
4. There are foci of "fresh" DDT related pollution despite the prohibition to use this compound.

Key-words: persistent organic pollutants, organochlorine pesticides, polychlorinated biphenyls, residual amounts, DDT, HCH, HCB, Heptachlor.

Environmental pollution by widely known Persistent Organic Pollutants (POPs) is nowadays an actual problem and the world community passed it to the XXI century. This challenge became an alarming theme for discussion at international assemblies and scientific forums, trade-union meetings and sittings of other social organizations.

The majority of organochlorine pesticides related to POPs are banned for use at the territory of Armenia since 1979s. Nevertheless, the residual amounts of organochlorine pesticides (DDT, DDE, lindane) continue to be found in different environmental media (soil, water), foodstuffs and even in breast milk samples.

For the first time a detailed monitoring of POPs content in different environmental media was performed within the Project "Enabling activities to facilitate early action on the implementation of the Stockholm Convention on Persistent Organic Pollutants (POPs) in the Republic of Armenia" Project (UNIDO). As a result of project implementation, 745 analyses were done. Samples of surface water, soil, bottom sediment, biomedia (breast milk) were analyzed for residues of organochlorine pesticides (n=469) and polychlorinated biphenyls (n=276).

The results of monitoring studies for determination of residual amounts of organochlorine pesticides revealed that residues of DDT, DDE, and γ-HCH (lindane) were identified with high frequency in environmental media, foodstuffs and human biomedia. According to monitoring-based data the frequency of POPs (lindane, DDE) determination in samples of breast milk of nursing mothers from rural regions (Arzgatsotn marz) made 87-97 %.
Studies for residual amounts of DDT and HCH in water of Sevan Lake, silt (sludge) and muscle tissues of fish revealed the following:

- DDT in water of Sevan Lake was identified on he average, at 0.0004 mg/l (Smaller Sevan) and 0.0003 mg/l (Bigger Sevan);
- In the silt (bottom sediment) DDT was determined at the level of 0.01-0.037 mg/kg, while HCH made 0.57-1.46 mg/kg;
- In muscle tissue of whitefish (sig)DDT was determined at the level of 0.2 mg/kg, DDE at 0.1 mg/kg and HCH at 0.2 mg/kg;
- In muscle tissue of khramulya fish that is fatter compared to sig DDT was determined at the level of 0.006 mg/kg, DDE at 0.027 mg/kg and HCH at 0.001 mg/kg (1980-1983).

The residual amounts of hexachlorobenzene (HCB) in environmental media were as follows;

- In surface waters HCB was revealed in the range of 0.005-0.056 mcg/l (2002-2003). The level of the mean content of HCB in water was in the range of 0.006-0.036 mcg/l.
- No HCB residues were identified in bottom sediments.
- In soils from transformer stations HCB was revealed in 1 sample and made 0.018 mcg/kg.
- In waste waters of sewage collectors HCB was revealed in 1 sample at the level of 0.016 mcg/l.

The residual amounts of HCB were also determined in samples of water from the water-supply system in Yerevan and Vanadzor. In the majority of drinking water samples taken in Yerevan (in 9 of 12) HCB was determined in the range of 0.0001-0.0078 mcg/l with the average content of 0.0028 mcg/l. In Vanadzor HCB residues averaged 0.005 mkg/l.
Monitoring of HCB in samples of foodstuffs taken in different marzes of Armenia indicated that

- In eggs HCB was revealed in the range of 0.008-4.54 mcg/kg. The average content made from 0.26 to 4.54 mcg/kg;
- In samples of meat HCB was determined in the range of 0.028-9.16 mcg/kg (on the average: 0.0072-2.73 mcg/kg);
- The residual amounts of HCB in milk were at the level of 0.009-0.74 mcg/l (on the average: 0.025-0.21 mcg/l);
- In sample of cheese HCB was revealed within the range of 0.1-15.65 mcg/kg, thus making on the average from 0.1 to 11.09 mcg/kg.

Monitoring-based data on determination of Heptachlor residual amounts in surface waters and foodstuffs (eggs, meat, milk and cheese) from different marzes of Armenia revealed that

- In surface water Heptachlor ranged 0.034-0.17 mcg/l (on the average the content of heptachlor made 0.074 mcg/l);

- o In eggs Heptachlor was determined at 0.006-0.04 mcg/kg;
- o In meat Heptachlor residues ranged 0.024-3.31 mcg/kg;
- o In samples of milk the average content of Heptachlor was 0.06-0.10 mcg/l;
- o In samples of cheese was not determined, exept 1 sample with residues level at 0.153 mcg/kg.

Monitoring of residual amounts of DDT (Σ DDT) in samples ofanimal origin foodstuffs (meat, eggs, milk and cheese) taken in different marzes of Armenia (Syunik, Ararat, Armavir, Aragatsotn and Lori marzes) demonstrated that DDT residues in eggs varied in the range of 0.48-6.03 mcg/kg; in samples of meat DDT levels were 1.1-5.24 mcg/kg; in samples of milk – 0.29-2.66 mcg/l; in samples of cheese DDT was found at 0.35-12.73 mcg/kg.

However, it is necessary to state that monitoring on contents of these substances in the environment is performed non-systematically, and in practice there are no data on quantitative and qualitative content of dioxin-containing releases of the majority of industrial enterprises.

The content of PCB in water and bottom sediment of certain rivers and Sevan Lake was studied. The results of PCB content in environmental media are presented below.
PCBs in soils of electrical stations of Hrazdan Hydropower plants made:

- at Hrazdan HPP: 86.12 mcg/kg (on the average; conditionally clean samples);
- at Argel HPP: 71.66 mcg/kg (on the average; conditionally clean samples) and 206.36 mcg/kg (on the average; evidently polluted samples);
- at Arzni HPP: 138.47 mcg/kg (on the average; conditionally clean samples) and 201.0 (on the average; evidently polluted samples);
- AT Kanaker HPP: 57.88 mcg/kg (on the average; conditionally clean samples).

The difference in PCB content revealed in different samples of soil taken in transformer facilities of Hrazdan and Vorotan cascades made 30 times. One can also state that PCB concentration considering from the initial point of pollution decreased with the distance, however the areal of pollution by them increases.
Similar results were also obtained in studies on soils from transformer stations at Thermal power plants. At Hrazdan TPP PCB levels in conditionally clean samples made 49.75-53.6 mcg/kg, whereas in evidently polluted samples PCBs reached 892.46 mcg/kg. At Vanadzor TPP only conditionally clean samples of soil were studied; on the average PCBs were determined at 86.75 mcg/kg. According to data obtained, it is possible to conclude that no significant difference was revealed in PCB-relate pollution of soils at TPPs and HPPs.

According to studies on PCBs in surface water from basins in the vicinity of HPP the content of PCBs on the average made 1.49 mcg/kg (in samples from Vorotan), while in water near Hrazdan HPP PCBs averaged 1.82 mcg/kg. If we take into consideration that at the water-catchment basin there were no major industrial enterprises, it is possible to suppose that the revealed concentration of PCB (1.49 mcg/kg) is a consequence of activity performed by HPPs functioning on Vorotan river. However results on water samples from rivers in no way connected with HPPs or industrial enterprises indicated that PCB concentration that was determined throughout did not differ depending on water basin characteristics. Such water reservoir as Pambak river flowing along the agricultural regions (up to Vanadzor town) is also polluted by PCB and on the average the level makes 1.74 mcg/kg.

In water of rivers from the catchment basin with major industrial enterprises (mining-and-smelting) PCB content never significantly differed from all the rest. Thus, in waters of Vokhchi and Debet rivers PCB content made 1.33 mcg/l and 0.68 mcg/l, appropriately.
In samples of water from Sevan Lake at the watershed of which there are no large-scale enterprises PCB content was at the level of 0.6 mcg/l, while in rivers feeding the lake PCBs make 0.68 mcg/l.

Residual amounts of PCB in bottom sediments of rivers were determined as follows:
- Vorotan river: 98.37 mcg/kg;
- Pambak river: 68.03 mcg/kg;
- Debet river: 719.06 mcg/kg.

On all probability, high PCB levels in bottom sediments of Debet river might be explained by chance, as in 11 of 12 samples PCBs made approximately up to 100 mcg/kg, whereas in 1 sample PCB reached 7897.076 mcg/kg. This latter conditioned the increase of PCB average content in water of Debet river.

PCB monitoring performed in concern of foodstuffs revealed that in eggs from different regions PCb, on the average, was determined at the level of 1.61-2.78 mcg/kg, in meat – 13.86-25 mcg/kg, in milk – 4.52-5.15 mcg/l, in cheese – 11.84-63.86. We can only suppose what polychlorinated biphenyls are revealed in the environment of Armenia, as the method of determination provides us with the total content of these substances. However, knowing the types of transformer oils obtained by our industry we can definitely define the types of PCBs. As usual these oils contained 2-chlorine-, 5-chlorine-, 3-chlorine containing biphenyls.

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DESIGN OF A NETWORK TO MONITOR THE CONTINENTAL AND INTERCONTINENTAL BACKGROUND OF PERSISTENT ORGANIC POLLUTANTS IN AFRICA

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Abstract
A network for the study of long-term trends of the continental background in Africa and the intercontinental background of persistent organic pollutants (POPs) as resulting from long-range transport is designed. The results of a pilot phase sampling programme in 2008 and climatological information from the period 1961–2007 were used to apply objective criteria for the selection of stations for the monitoring network. Out of 26 original stations some have been rejected either because of suggested strong local POP sources or because of local meteorological effects, which may prevent long-range transported air to reach the sampling site. The representativeness of the meteorological patterns during the pilot phase with respect to climatology was assessed by comparison of climatological vs. observed wind roses and by comparison of backward trajectories with the climatological wind (NCEP/NCAR re-analyses). With minor exceptions advection to nine checked stations in 2008 was typical for present-day climate. Six to nine stations would cover satisfyingly large and medium to densely populated regions of north-eastern, western and eastern Africa and neighbouring seas. Among the densely populated areas of the continent, only southern Cameroon, parts of the Abyssinian plateau and most of the Great Lakes area would not be covered. The potential of the network is not hampered by ongoing long-term changes of the advection to the selected stations, as these do hardly affect the coverage of target areas.

Key-words
monitoring network, persistent organic pollutants, long-range transport, climatology, Africa

Introduction
The aim of the Stockholm Convention on POPs is to „protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically and accumulate in the fatty tissue of humans and wildlife.“[1] Therefore, measures to eliminate or reduce the emission of POPs into the environment are needed.[1] Furthermore, as due to long-range transport not only source areas with substance application or production are put at risk, regional surveillance of the environment is required. The motivation of this study is to create a network for control of POP levels in air on the regional scale, i.e. in the continental background of Africa as well as in intercontinental transport towards Africa. At present no such network exists. The mission of suggested network is to cover the long-term trends and eventually episodic events. In consequence of

economic limitations the network should be small, i.e. not including more than 10 stations. This paper describes the application of objective criteria to 26 candidate sampling sites from a pilot phase to select a short list of suitable network stations, based on a combination of the pilot phase sampling programme results, meteorological and climatological information.

Data and methods

Sampling

During the pilot phase samples were collected at 26 stations in 15 countries throughout the continent. Passive air samplers (PAS) are simple and do not need electricity for operation, therefore are suitable for long-term monitoring at background sites with limited or none technical equipment. Limited time resolution of PAS does not hamper long-term background monitoring. Passive air samples equipped with a polyurethane foam disk were collected as 28-day means (some exceptions were in the range 25–33 days) and afterwards analysed according to standard operational procedures.

Back-trajectories

Three-dimensional 96-hours back-trajectories were used to identify the geographical origin of air advected to individual sites during the whole year 2008 (starting every 4 hours 200 m above ground, HYSPLIT model[2]). The chosen arrival height ensures starting of the back-trajectory within the planetary boundary layer, which was verified for each case.

Climatological analysis

NCEP/NCAR re-analysis data[3] were used to characterize wind direction patterns of individual sites. For each station the four closest grid points were identified (spatial resolution of the database is 2.5° latitude x 2.5° longitude) and interpolated. The resulting database comprised six-hourly wind direction data on the 1000, 925 and 850 hPa levels for the period 1961–2007. Changes in mean wind roses with height (individual pressure levels) were evaluated which led to a decision to use the closest pressure level to the starting level of the back-trajectories for further analysis. For the Mt. Kenya station, 3678 m a.s.l., the pressure level of 600 hPa was chosen.

Selection of suitable network stations

A number of criteria was applied to come up with a reasonably small number of stations for the continental monitoring network. The reduction of number of stations proceeds in several steps[4]: (1) All stations had been sorted by allocation and with respect to individual contaminants to four types of sites – pristine environment, continental background site, moderately polluted (rural or residential) and heavily polluted (urban or industrial) environment. The latter category included stations for which the results of the pilot sampling phase indicate strong local sources of more than one POP. These were rejected. (2) Local meteorological phenomena may prevent long-range transported air to reach the surface sampling site. This may be caused by local meteorological factors, e.g. frequent low-laying cloud cover, frequent precipitation. Also, when the station is situated within a local wind system (e.g. land–sea breeze or mountain slope circulation), the collected air would involve more likely local than regional sources. (3) Stations of the same type of site with similar origin of advected air were excluded, based on back-trajectories for the year 2008 in combination with respect to local pollution sources. Upon application of these criteria, 1-3, a candidate list with nine stations remained: Tunis (Tunisia), Khartoum (Sudan), Tombouctou (Mali), Sheda (Nigeria), Asela (Ethiopia), Mt. Kenya (Kenya), Lusaka International Airport (Zambia), Reduit (Mauritius) and Molopo (Republic of South Africa). To these pre-selected stations climatological analysis was applied.

Analysis of wind patterns

Wind direction frequencies and their seasonality were characterized by monthly mean wind roses for each station and each month of the period 1961–2007. However, when two (exceptionally more) different directions of comparable frequency are found, the characteristics derived from wind roses can be considerably problematic. In such cases, the wind direction can be more correctly described using the prevailing wind direction (PWD), with its frequency (PWF) calculated according to Nosek[5].

In general, wind patterns at each site are affected by the geographical location (latitude and longitude) and the general atmospheric circulation of the respective region. For example Tunis is located in subtropical area and its wind patterns are influenced by movement of the climatological front between moderate and tropical air masses. This leads to greater variability in wind directions during the year and also during individual months (Fig. 1a). In contrast, Sheda is located close to the equator in an area advected by trade winds from opposite directions in response to the seasonally varying location of the intertropical trough (Fig. 1c).

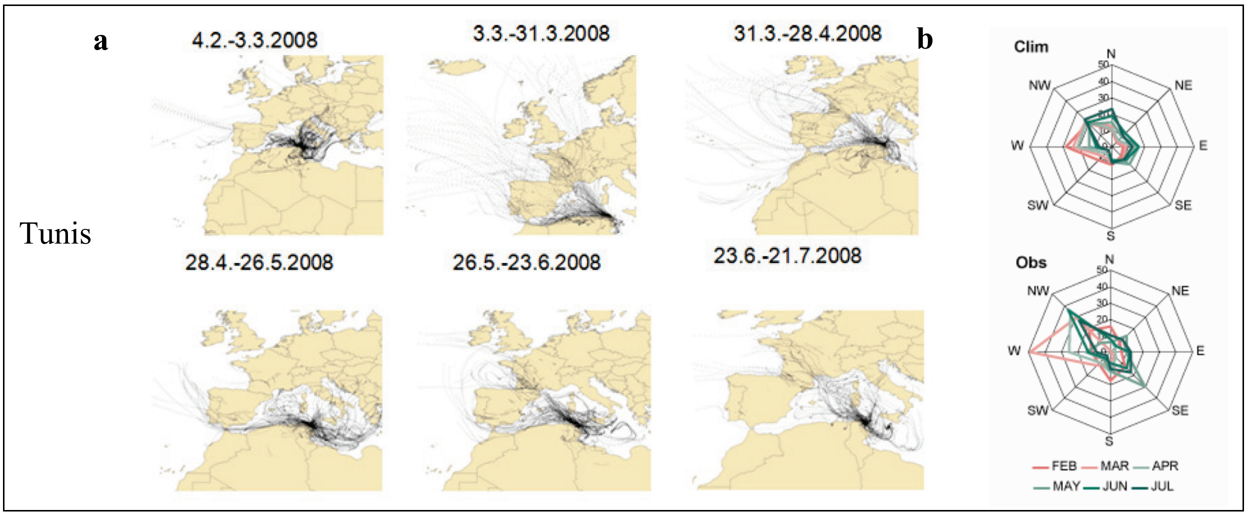

Fig. 1 Back trajectories (96 hours back, starting every 4 hours, arrival height 200 m above ground) for individual sampling intervals for Tunis (a) and Sheda (c) stations. Mean wind roses calculated from re-analysis data for the period 1961–2007 (above) and from back-trajectories (one hour back, 200 m above ground; down) for Tunis (b) and Sheda stations (d)

From NCEP/NCAR re-analysis data derived wind roses were then compared with wind roses derived from the back-trajectories (last hour before arrival) to determine to which extent the advection patterns during the pilot phase (in the year 2008) reflected the climatological advection (in the period 1961–2007). An example for this comparison shows Fig. 1b, d. Tunis is a station where both types of wind roses are in general good agreement, both with regard to prevailing wind directions and overall patterns. In opposite of this, Sheda shows less correspondence between climatology and back-trajectories, especially for April to June when climatology shows clear domination of south-western winds, whereas for the back-trajectories southern directions are slightly prevailing.

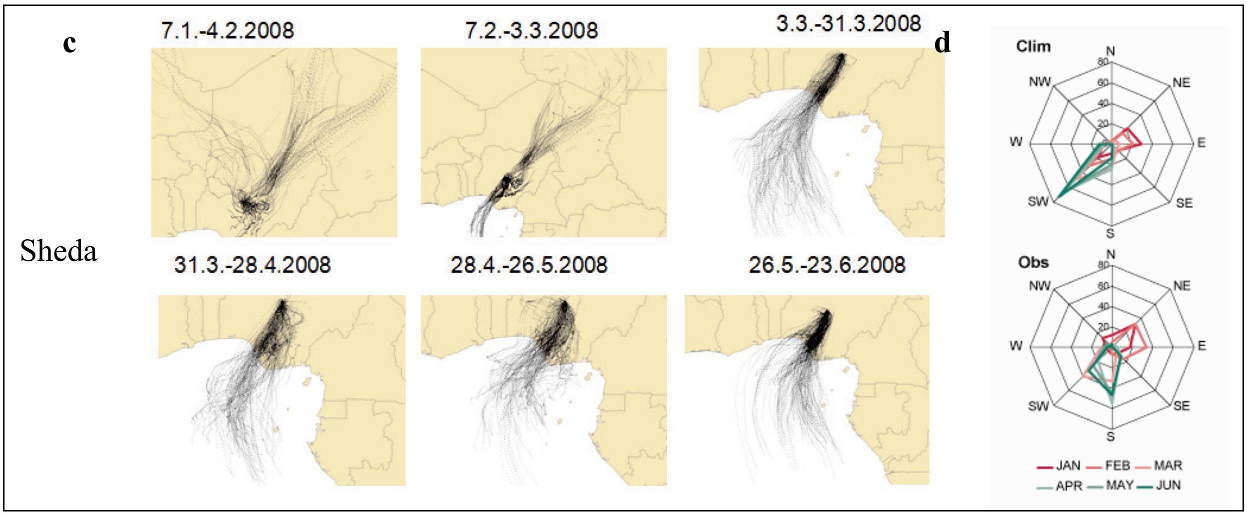

Fig. 1 Continued

It is found that all stations keep similar overall patterns and differ only in some months and these differences refer to adjacent directions (as for Sheda south-west vs. south) and thus can be interpreted as random (back-trajectories were used only for one year which increase variability). For this reason, the advection during the pilot phase of the sampling programme can be considered as climatological for all stations and no station had to be rejected after this analysis.

PWD was also used to analyse the temporal stability of wind patterns. The PWD linear trend and its significance were calculated for each station and month. A significant trend would suggest changes to be expected in the near future. This could influence the geographical coverage of the suggested monitoring network. Three stations (Tombouctou, Tunis and Reduit) show very stable airflow patterns. All the other sites suggest in minor or even large parts of the year significant changes. It is found, however, that these are either not influencing or even improving the geographical coverage of the network.

Regions expectedly covered by suggested monitoring network

The remaining stations cover rather satisfyingly large and important regions of Africa and its neighbouring seas[4]. Nevertheless, some areas would not be covered (Fig. 2), especially in central and south-western parts of Africa which are less populated, but also some more populated areas as southern Cameroon, parts of the Abyssinian plateau or the Great Lakes area.

Based on all above mentioned considerations, a list of six essential stations includes Tunis, Tombouctou, Sheda, Khartoum, Mt. Kenya and Molopo. Lusaka, Asela and Reduit are stations somewhat less significant in terms of spatial and temporal monitoring and, hence, for the performance of the network[4].

Conclusions

After applying a number of objective criteria, a small number of stations (6-9 stations) is suggested for the continental monitoring network. These would cover most and substantial parts of Africa and neighbouring seas, but would also exclude some parts. The analysis of airflow patterns for nine stations during the 1961–2007 period illustrated low inter-annual variability, but identified significant ongoing changes of the circulation patterns over Africa which could partly change the long-range transport and detectable sources of air contamination at the selected stations. However, no eventually corresponding significant losses of regions covered by the suggested monitoring network are indicated by now[4].

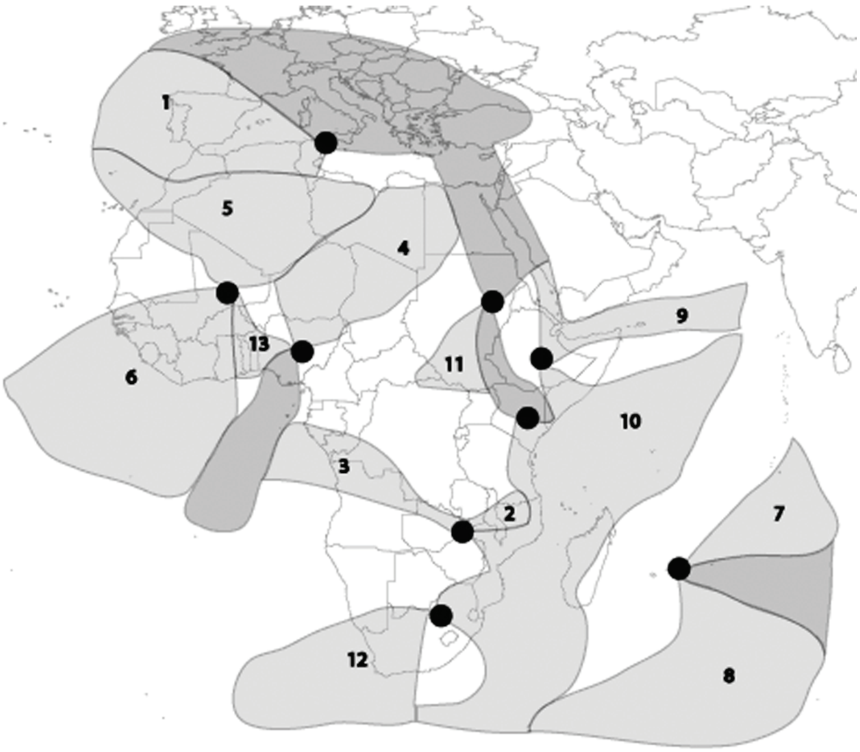

Fig. 2 Coverage of the monitoring network: Sectors covered by advection to 9 stations in the year 2008. Key: Dark shading = throughout the year; pale shadings: 1 = November to April, 2 = August to October; 3 = December to January; 4 = November to February; 5 = October to April; 6 = July to October; 7 = January to March; 8 = May to September; 9 = October to April; 10 = November to March, 11 = April to September; 12 = June to August, 13 = September to October only, respectively.

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LONG-RANGE TRANSPORT OF PERSISTENT ORGANIC POLLUTANTS TO THE REGIONAL OBSERVATORY KOŠETICE, CZECH REPUBLIC

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Abstract
A continuous monitoring campaign at the background site Košetice, Czech Republic, provides a unique dataset. Air mass back trajectories were generated for ambient air samples taken in 1997-99 and 2004-06. Resulting maps demonstrating the spatial distribution of mean ground source loadings were compared quantitatively and qualitatively to determine temporal and spatial trends in emission characteristics. This study presents a transport pathway analysis tool that can facilitate the detection and interpretation of trends in persistent organic pollutant (POP) air concentrations at background monitoring sites as recommended by the Global Monitoring Plan for POPs under the Stockholm Convention.

Keywords
Persistent organic pollutants, background monitoring site, long-range transport, air mass trajectories, temporal and spatial trends in emissions

Introduction
The aim of the Global Monitoring Plan (GMP) for POPs under the Stockholm Convention is the development and implementation of arrangements to provide comparable monitoring information on the presence of chemicals listed in Annexes A, B and C of the Convention as well as their regional and global environmental transport. Results will be used to determine trends from monitoring of POPs globally to support the effectiveness evaluation of the Convention. Ambient air was chosen as an important matrix due to its very short response time to changes in atmospheric emissions and relatively well-mixed character. Further, it is an entry point into food chains and a global transport medium (UNEP, 2007). According to the GMP, air mass trajectories are a useful tool for the evaluation of regional and global transport pathways.

Ambient air POP concentration data from the background observatory Košetice, central Czech Republic, are used in this study. This observatory is a part of the EMEP (European Monitoring and Evaluation Programme) network, GAW (Global Atmosphere Watch) and various national and international monitoring programmes (Holoubek et al., 2007). The here presented study is focused on organochlorine pesticides (DDT and its metabolites; α- and γ-hexachlorocyclohexane, HCH; hexachlorobenzene, HCB) and selected polychlorinated biphenyls (PCB52, PCB153).

Method
The periods 1997-99 amd 2004-06 were chosen to be suitable to study a decadal trend in emissions. Details on the sampling techniques, chemical analysis and quality control/quality assurance applied for air samples taken in Košetice can be found in Holoubek et al. (2007).

Threedimensional air mass back trajectories were generated using the HYSPLIT model (Draxler and Rolph, 2003). Eight trajectories per 24 hour sample were calculated 96 hours back in time at a starting height of 500 m above ground level. To ensure the condition of a well mixed atmospheric boundary layer (ABL) with dominating advection, trajectories starting during an inversion lower than 500 m altitude above ground were excluded from the analysis (inversions occured mostly during winter months). As relevant pollutant sources are mainly in the ABL, trajectory segments above this layer were also excluded from the analysis.

Hourly trajectory segment endpoints were all sorted onto a geographical 0.25 × 0.25 cell grid encompassing Europe and the adjacent seas using a GIS software (ArcView). The mean ground source loading, a continuous measure for the influence of ground surface emissions on the composition of passing air masses (Lammel et al., 2003) was calculated in each grid cell:

$$L_g = \sum_{i=1}^{I}\sum_{j=0}^{96} \frac{c_{ij}\left[1-(h_{ij}/96)\right]}{n_g} L_0$$

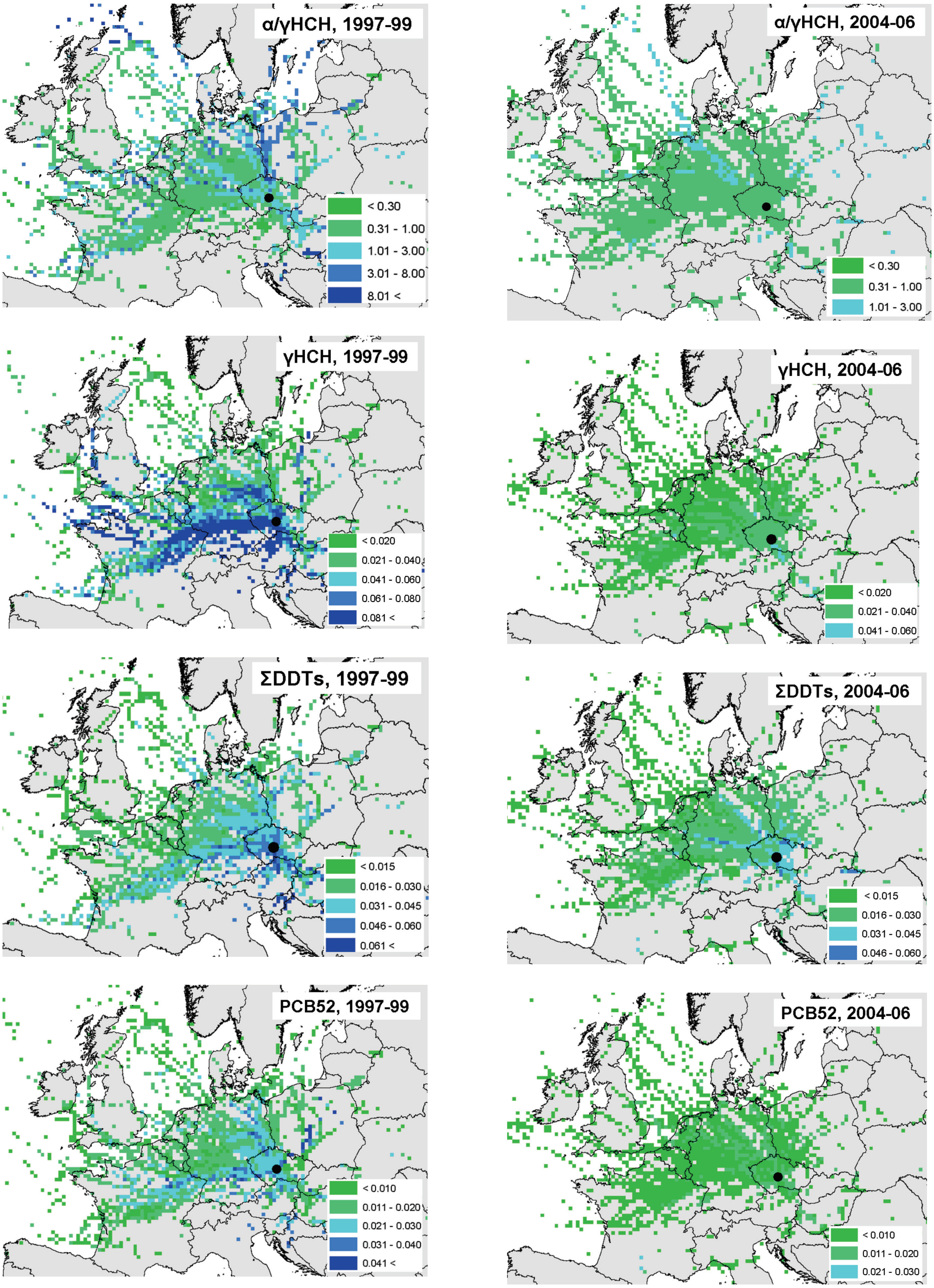
where I is the total number of trajectories; c_{ij} the total atmospheric concentration of pollutant at the receptor site upon arrival of the i^{th} trajectory; n_g the total number of trajectory hourly points in grid cell g; h_{ij} the number of hours counted back from arrival time for the j^{th} hourly point, i^{th} trajectory; $1-(h_{ij}/96)$ are time weights of hourly points and L_0 the unit loading of surface sources to air mass, set equal to 1 for trajectory hourly points which fall into grid cell g and set equal to 0 for all other trajectory hourly points.

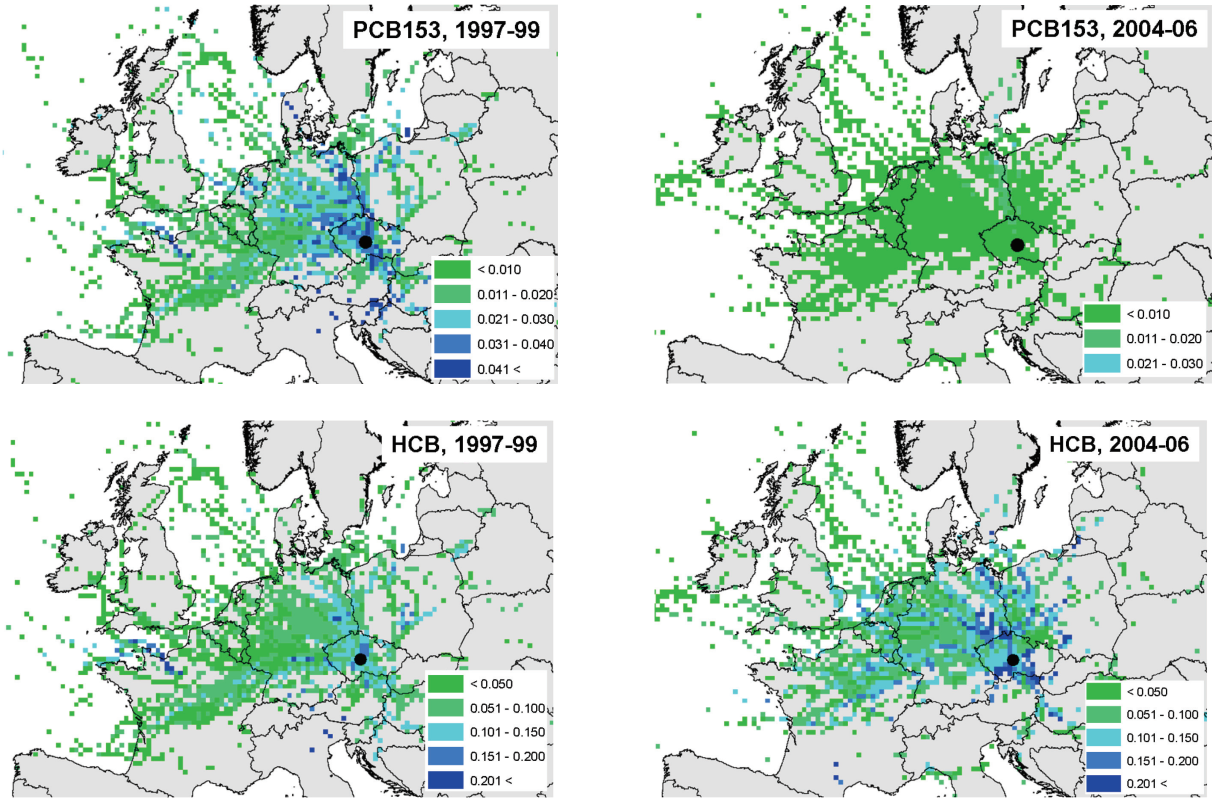
The two studied time periods are compared in both a quantitative (relative contribution of selected countries to air pollution in Košetice) and qualitative (calculation of centres of gravity in two geographical sectors; Lee and Wong, 2001) manner and the results are validated against known pollutant source areas. To address HCH origin, also the loading to a ratio of α-HCH/γ-HCH, is plotted. A more detailed description of both approaches can be found in Dvorská et al. (2009).

Results

The spatial distribution of ground source loadings is presented in Fig. 1. Concentrations of all studied pollutants transported by air to Košetice between 1997 and 2006 decreased, with the exemption of HCB. The rise in HCB emissions can be at least partly explained by floods in the Danube watershed in 2002. Emissions significant in 1997-99, which subsequently significantly decreased, were found in France (lindane), western Poland, Hungary and the north of former Yugoslovia (technical HCH) and the Czech republic (DDT). In 2004-06 significant emissions were still found in the north of Czech republic (DDT and HCB) and Germany (PCBs and HCB).

Figure 1 Distribution of ground source loadings L_g for studied persistent organic pollutants in both studied periods. The black dot depicts the position of Košetice.


α/γHCH, 1997-99
< 0.30
0.31 - 1.00
1.01 - 3.00
3.01 - 8.00
8.01 <
α/γHCH, 2004-06
< 0.30
0.31 - 1.00
1.01 - 3.00
γHCH, 1997-99
< 0.020
0.021 - 0.040
0.041 - 0.060
0.061 - 0.080
0.081 <
γHCH, 2004-06
< 0.020
0.021 - 0.040
0.041 - 0.060
ΣDDTs, 1997-99
< 0.015
0.016 - 0.030
0.031 - 0.045
0.046 - 0.060
0.061 <
ΣDDTs, 2004-06
< 0.015
0.016 - 0.030
0.031 - 0.045
0.046 - 0.060
PCB52, 1997-99
< 0.010
0.011 - 0.020
0.021 - 0.030
0.031 - 0.040
0.041 <
PCB52, 2004-06
< 0.010
0.011 - 0.020
0.021 - 0.030



The major contributors to the total burden of selected POPs in Košetice air are the neighbouring countries together with France, a major consumer of lindane in the past (Holoubek et al., 2000; Table 1). Spatial shifts in the positions of potential source areas in the two studied periods were found for lindane, the sum of DDT and its metabolites and PCB52. A more detailed discussion on the results can be found in Dvorská et al. (2009).

Table 1 Relative contribution (in %) of selected countries contributing to the total POP burden in Košetice air

Country	γHCH		HCB		ΣDDTs		PCB52		PCB153	
	97-99	04-06	97-99	04-06	97-99	04-06	97-99	04-06	97-99	04-06
Germany	31	32	33	35	33	34	34	37	37	38
France	28	19	20	18	20	17	23	15	16	15
Austria	10	4	5	3	6	3	5	3	5	<3
Poland	5	13	12	14	10	15	10	14	10	15
Czech Rep.	9	11	11	10	11	11	9	10	11	10

Conclusions

As presented here, receptor models based on air mass back trajectories may contribute to the (1) determination of potential known and unknown source areas affecting substance concentrations at the site of air quality measurement, (2) first description of potential sources, which may be inventorised after their verification, determination of appropriate emission factors and, therefore, contribute to the definition of effective measures of air pollution control, (3) explanation of fluctuations and concentration levels measured at background sites and their temporal trends and (4) description of changes in intensity and location of potential sources areas in time.

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HCHs ACCUMULATED IN MACROINVERTEBRATES IN THE ELBE RIVER BASIN TWO DECADES AFTER THE END OF THEIR PRODUCTION

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In the 2nd half of the 20th century, HCH was widely produced in the Elbe River catchment. During spring and autumn 2008, selected macroinvertebrate species were investigated in the Elbe River and tributary in order to quantify the concentration levels of HCH isomers at the lower trophic level.

The prohibition of the application of lindane (γ-HCH) for agricultural use in the Elbe basin region more than one decade ago, has resulted in currently only slightly elevated concentration of γ-HCH, which does not seem to be site dependent, whereas the more resistant by-products α-, β-, δ-, and ε-HCH differed significantly along the longitudinal profile. In general, lower values of these isomers were observed at all Czech sites compared with those in Germany. At the most contaminated site Spittelwasser (a Mulde tributary), five order higher values were recorded (up to 234 μg kg^{-1} ww α-HCH in Hydropsychidae or 162 μg kg^{-1} ww β-HCH in Hydropsychidae) than at the Czech reference site Verdek (<0,01 μg kg^{-1} ww in Hydropsychidae and Asellus aquaticus). The Obříství site influenced by the Spolana Neratovice chemical plant had only negligibly elevated values. A comparison of measured values with data obtained by UBA did not show evidence of possible biomagnification.

Key words: HCH isomers, freshwater macroinvertebrates, Elbe River, bioaccumulation, biomagnification

Background

In the 2nd half of the 20th century, lindane (γ-hexachlorcyclohexan) was widely used as an insecticide both in agriculture and in forestry. The manufacturing process of lindane resulted in up to 90% of the unwanted waste “by-products” α-, β-, δ-, ε-HCH isomers, which are more resistant to degradation [1].

From the early 1960s up to the late 1980s lindane was produced in large amounts in the Elbe basin, mainly in the Bitterfeld region in Germany and on the Czech side at the SPOLANA Neratovice chemical plant. The total amounts of lindane produced in Spolana from 1961 – 1972 are estimated as approx. 3300 t HCHs [2]. The waste was disposed at Hájek near Karlovy Vary and was partly burned. One of three contaminated buildings in the Spolana factory ended up in a concrete sarcophagus, and the other two will be de-contaminated by chemical decomposition [3] In the Bitterfeld factory more than 150 000 t/a was produced between 1950 – 1982 [4]. The waste water was drained into Spittelwasser brook which flows into the Mulde River, a tributary of the Elbe River. The solid waste was deposited in the landfills „Antonie“ and „Freiheit“ in the immediate vicinity of the chemical plant. In FALIMA Magdeburg, 5645 t of lindane was processed from imported tech. HCH from 1967 – 1981 [1]. The ballast isomers were disposed of in the landfill „Emden“.

Investigations of bream fish (*Abramis brama*) by the Federal Environment Agency of Germany (UBA) in the Mulde River demonstrated temporary extreme contaminations by HCH in 2004 and 2005 [5]. For fish, macroinvertebrates are an important component of their food. Therefore, the recent HCH accumulation level in freshwater benthic fauna of the Elbe River catchment was investigated to define the ecological risk at a lower trophic level, with emphasis on differences between individual HCH isomers.

Results and discussion

During spring and autumn 2008, selected macroinvertebrate species were sampled at 6 locations in the Elbe River in both the Czech Republic and Germany, and 2 locations in the Mulde and Spittelwasser tributaries in Germany (Fig 1.).

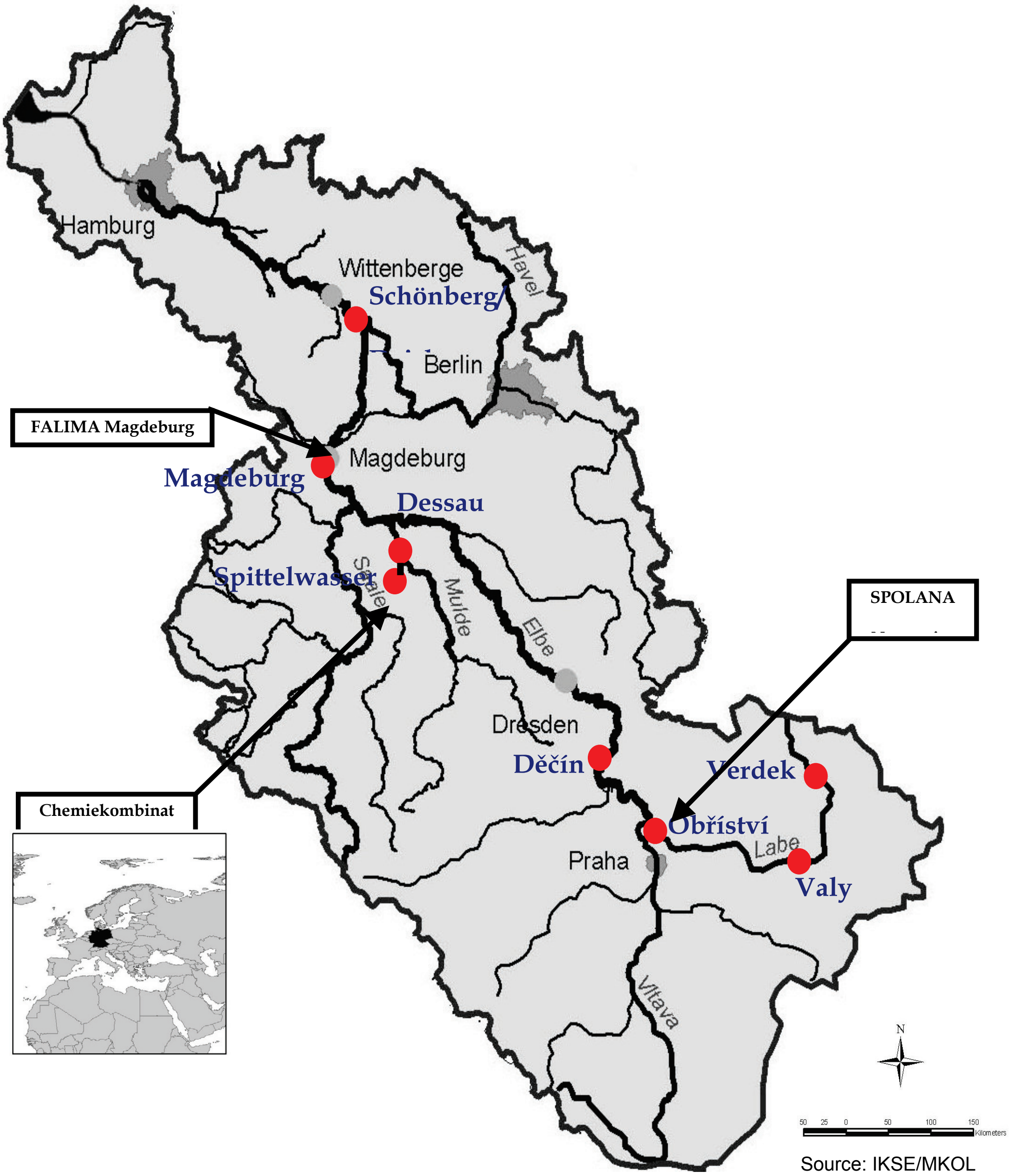

Fig 1. Investigated sites in the Elbe River basin (CZ/D) (red dots)

The following groups of macroinvertebrates were investigated: crustaceans, caddisflies, mayflies, dragonflies, leeches and molluscs. At each site, from 1 to 4 of these groups were analyzed for HCHs.

Local variations

In general, lower values of all isomers were observed at all Czech sites (< 1 µg/kg wet weight) compared with those in Germany. At the most contaminated site Spittelwasser (the Mulde tributary), five order higher values than at the Czech reference site Verdek were measured.

Generally, only slightly elevated concentrations of **γ-HCH** were found, except for Spittelwasser (Fig. 2). Gamma-HCH values didn't seem to be site dependent, whereas the more resistant by-products differed significantly along the longitudinal profile: **α-, β-, δ-, and ε-HCH** showed very similar site variations with diverse value ranges. The highest concentrations were revealed for β- and α-HCH. This occurrence of waste isomers in environment indicates the former use of technical HCH (mixture of all isomers) or is typical for former HCH production sites. In contrast, higher levels of γ-HCH should reflect **lindane** (>99% γ-HCH) applications in the past [1]. Among investigated Czech sites, only the Obříství site influenced by Spolana Neratovice had elevated waste isomer levels, and these were still practically negligible. On the other hand, at the most contaminated Spittelwasser site, the influence of former HCH production in Bitterfeld is clearly seen, with traces also present far downstream.

The prohibition of the application of lindane (γ-HCH) in agriculture and forestry in the Elbe basin region more than one decade ago seems to have resulted in there being only slightly elevated concentrations of γ-HCH at present. However, as can be seen in the Bitterfeld region, the more resistant by-products still persist, and pollution of the water ecosystem including macroinvertebrates can still occur.

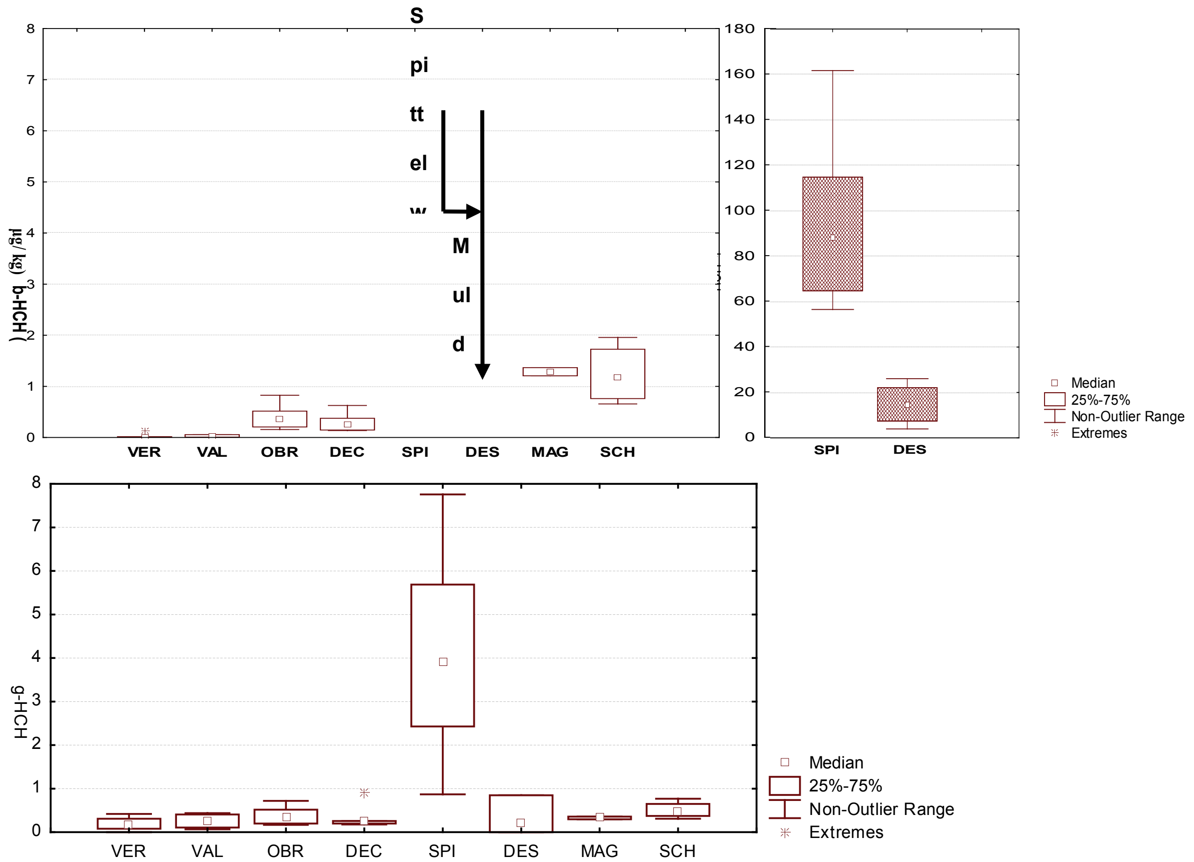

Fig. 2 Beta- and gamma-HCH concentrations in invertebrates along the longitudinal profile of the Elbe River and tributaries (µg/kg ww)

HCH isomers

The percent ratio of particular isomers, as mentioned above, gives in large extent temporary or causal information about source of contamination. At Spittelwasser site dominated strongly waste isomers, whereas γ-HCH was ranged in very low percentage, as can be seen at Fig. 3 and Fig. 4. Generally, γ-HCH had higher percentage at sites not affected or few affected by industrial production.

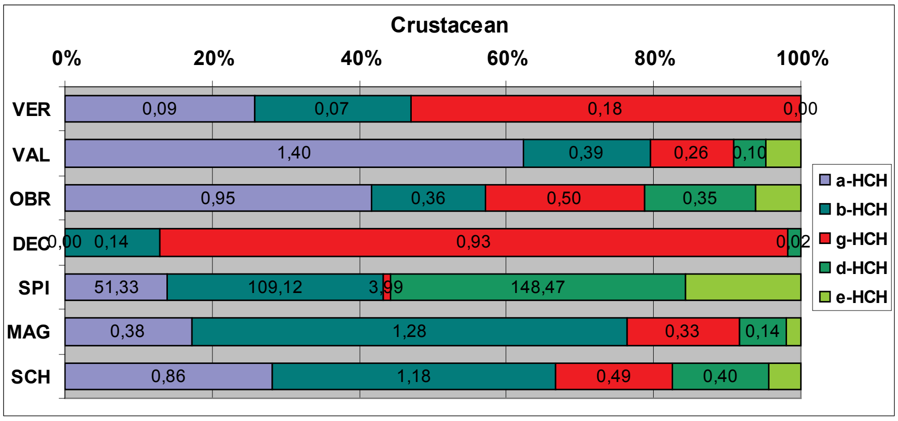

Fig. 3 HCH isomers concentration in crustaceans (Crustacea)

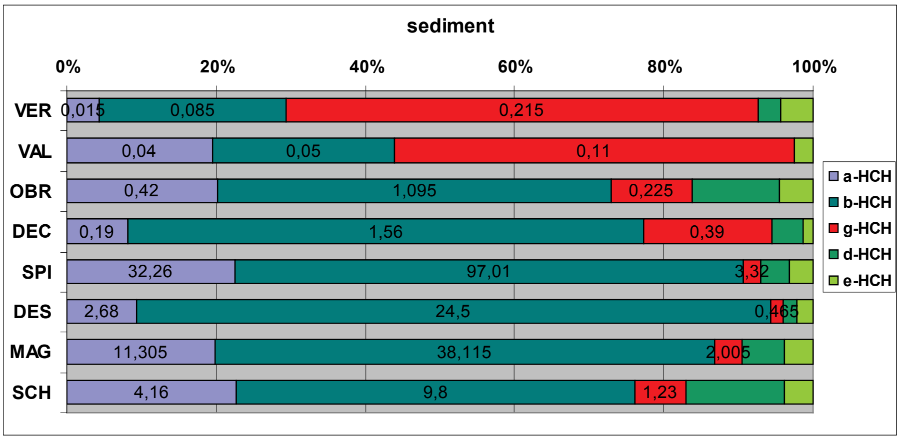

Fig. 4 HCH isomers concentration in surface sediment samples

Biomagnification

The phenomenon when a contaminant concentration in an organism increases within the food web is called biomagnification. As this phenomenon might be expected between macroinvertebrates and fish, we compared HCH isomer concentration data in macroinvertebrates and fish. HCHs accumulated in bream fish (Abramis brama) has been investigated by the Federal Environment Agency of Germany (UBA) in the Dessau/Mulde River since 1994. A temporary extreme contamination was found in 2004 and 2005, probably due to large flood in 2002, with concentrations exceeding the highest allowed values according to Residue regulation by 18-fold or 5-fold, respectively (Anonymous, 2006)

In 2008, a comparison of the data obtained by UBA with our data from the same locality showed values to be in the same range (Fig. 5). Thus, there was no evidence of biomagnification at this site.

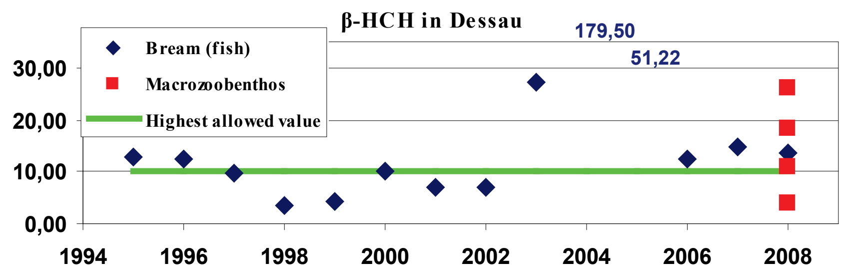

Fig 5. Beta-HCH concentrations (µg/kg ww) compared in bream (*Abramis brama*) and macroinvertebrates (*Ephemeroptera* and *Hydropsychidae*) in the Mulde River in Dessau

Conclusion

Despite the production of HCH in case area was abandoned more than 20 years ago and the use of lindane was strongly restricted more than 10 years ago, in the Elbe River catchment HCH isomers can be still detected in aquatic components. For a more complete research of the river ecosystem and better understanding the process of bioaccumulation is necessary to investigate as much compartments as possible. Thus, it is not suitable only to determine fish body burden but also macroinvertebrates as an important component of their food. However, there are not any publicized data about HCH bioaccumulation in macroinvertebrates in other European rivers. We examined several localities in the Elbe River catchment with different industrial history and exploitation. The contamination levels in macroinvertebrates differed significantly among investigated sites. We suggest these data could serve as reference data for further research. Whereas the isomer concentrations < 1 µg/kg ww can be considered as "background" values valid for common anthropogenic affected river, higher values indicate actual source of contamination, whether primary or secondary one.

Short summaries:

- ❑ The prohibition of lindane (γ-HCH) application in agriculture and forestry in the Elbe basin region more than a decade ago has resulted in there being only slightly elevated present concentrations of γ-HCH. On the other hand, the more resistant by-products still persist and pollution of the water ecosystem including macroinvertebrates still occurs.
- ❑ Only the Obříství site influenced by Spolana Neratovice showed elevated, though still negligible, values, whereas former HCH production in Bitterfeld enterprise has left traces far downstream.
- ❑ From our data in the Mulde tributary, there was no evidence of biomagnification.

Acknowledgments

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ORGANOCHLORINE PESTICIDES IN HUMAN MILK AS INDICATORS OF ENVIRONMENTAL POLLUTION

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Abstract

Among a large number of man-made chemicals, greater attention has been focused on semi-volatile and persistent organochlorines, such as DDT and its metabolites, HCH and isomers, heptachlor, aldrin, and possible degradation products. Due to their widespread use, organochlorine pesticides (OCPs) can be determined in all environmental matrices, biotic and abiotic. Humans, particularly young infants, are exposed to these chemicals, bioaccumulated and biomagnifed through food chain. Measurements of OCPs (4,4-DDT, 4,4-DDD, 4,4-DDE, aldrin, endrin, endosulfan I and II, endolulfan sulfate, dieldrin, endrinaldechyde, heptachlor and α-, β-, γ – HCH) in milk samples of 22 healthy mothers were performed in sampling campaign 2006, in surrounding area of Novi Sad. Determination and detection were realized by GC-ECD (HP 5890). Estimated daily intake of pesticide residues by an average 3,5 kg newborn on the 3rd day of life via colostrum, collected in 2006, was compared with estimated daily intake via colostrum collected in 2003, in the same area and under the same curcumstances. The fall of DDE estimated intake was observed, while DDT estimated intake increased significantly. α-HCH estimated intake increased, but β- and γ – HCH was below the level of detection. All other pesticide chemicals were for the first time measured in colostrum in Vojvodina region. Since biotransformation and metabolism of DDT are slow processes, its significantly higher concentrations in 2006 colostrum, imply the negative DDT balance in examine milk samples which points out recent input of DDT in environment. The most lipophilic character of DDE causes the more stores of DDE in human being than other DDT metabolites, hence, the rise of DDE is expected in future, as the consequence of this recent DDT environmental influx. Human milk, was once again a mirror of environmental pollution.

Key-words

organochlorine pesticides, human milk, environmental pollution, DDT, HCH

Introduction

The progress of the chemical industry in the past century has supplied the world with a vast amount of chemicals, especially organic chemicals which are characterized by specific physical, chemical and technical performances and therefore these chemicals were and are frequently used, as well as pesticides (insecticides, herbicides and others). Among a large number of man-made chemicals, greater attention has been focused on semi-volatile and persistent organochlorines, such as DDT and its metabolites, HCH and isomers, heptachlor, aldrin, and possible degradation products.

Organochlorine pesticides (OCPs) are used to control weeds, insects, and other organisms in a wide variety of agricultural and non-agricultural settings. Due to their widespread use, OCPs can be determined in all environmental matrices, biotic and abiotic.

Different groups of population are exposed to pesticides in several ways and in varying degrees such as occupational and non-occupational exposure. The occupational exposure could be during manufacture and formulation of pesticides in industrial settings and their distribution in field condition during application of pesticides. The non-occupational exposure (or) indirect toxic effects may be due to pollution of the ecosystem or habitat as a whole such as from water, air and food.

These lipophlic OCPs, with high resistance to degradation and long half-lives in humans, have been confirmed to bioaccumulate in blood, breast milk, and adipose tissues of humans through dietary intake (Smith and Gangolli, 2002). Exposure to OCPs, particularly to dichlorodiphenyltrichloroethane (DDT) and its metabolites has been associated with adverse health effects, including neurodevelopmental delay (Ribas-Fito´ et al., 2003), reproductive effects (Dalvie et al., 2004), preterm and small-for-gestational-age babies (Longnecker et al., 2001), and immunotoxicity (Cooper et al., 2004).

In response to the adverse effects seen in wildlife and humans, the production and use of OCPs were restricted and banned in Europe and North America during the 1970s and, consequently, the levels of OCPs in humans are now decreasing (Norén and Meironyté, 2000). Since milk is the only way for their excretion, the neonate, relying fully on mother's milk, as the only source of nutrients, may be at greatest risk of all mammals, particularly in the earliest neonatal period. Studies on OCPs in early human milk (colostrum) are few (Czaja et al., 1997, Vukavic et al., 1997, Vukavic et al., 2008).

Monitoring of OC pesticide residues (DDT with metabolites and α-, β-, γ-hexachlorocyclohexane isomers) in South Bačka started in 1982 (Vukavic et al., 1986). For last measurements, diferent group of OC pesticide residues, except for DDT, metabolites and α-, β-, γ- HCH, were chosen: aldrin, endrin, endosulfan I, endolulfan sulfate, dieldrin, endrinaldechyde, heptachlor and endosulfan II in samples of early human milk (3rd day lactation).

Material and methods

Donors of 3rd day colostrum were 22 healthy mothers living in and around the city of Novi Sad, who gave birth to healthy babies after a normal pregnancy and normal delivery in 2006. They filled in the questionnaire contained data on food habits, smoking, occupation and exposure to chemicals.

Mothers expressed colostrum in the amount of 21.87 ± 13.53 mL ($\overline{X} \pm SD$), range 7-55 mL, into specially prepared glass containers, on the 3rd postpartal day, after the 2nd morning breastfeed. Samples were frozen at -20°C until analyzed. After extraction, samples were analyzed using GC-ECD (HP 5890 supplied with a Quadrex fused silica column 5% Ph for OCPs.

Analytical determinations of OCPs (4,4-DDT, 4,4-DDD, 4,4-DDE, aldrin, endrin, endosulfan I, endolulfan sulfate, dieldrin, endrinaldechyde, heptachlor, endosulfan II and α-, β-, γ - HCH) in human milk samples were performed in the Analytical Laboratory at the Institute of Occupational Health in Novi Sad.

Results

Median values of concentrations (ng/mL) of OCPs detected in human milk are presented in Table 1. Aldrin (3.88, 4.99), endrin (4.74, 6.72) and 4,4-DDT (4.61, 4.53) were founded in highest concentrations (ng/mL - mean, SD) in human milk.

Table 1. Median values of concentrations (ng/mL) of OCPs detected in human milk

Chemical compound	COLOSTRUM		
	$\overline{X}$	SD	Range
Aldrin	**3.88**	**5.00**	0.49-24.85
Endrin	**4.74**	**6.72**	0.10-21.84
Endosulfan I	**0.21**	**0.28**	0.56-0.95
4,4-DDD	**3.12**	**4.53**	0.06-14.44
4,4-DDT	**4.61**	**10.37**	0.13-46.60
4,4-DDE	**2.52**	**1.42**	1.52-3.53
Endolulfan sulfate	**0.85**	**0.82**	0.11-2.61
Dieldrin	**0.15**	**0.10**	0.03-0.23
Endrinaldechyde	**0.50**	**0.41**	0.10-0.93
Heptachlor	**2.36**	**3.92**	0.31-10.30
Endosulfan II	**0.59**	**0.55**	0.14-1.58
α-HCH	**0.35**	**0.26**	0.08-0.79
β-HCH	**-**	**-**	-
γ-HCH	**-**	**-**	-

Average daily intake of pesticide residues per kilogram of body weight, through breast feeding, by an average, 3.5 kg newborn with an average intake of 60 ml/kg on the 3[rd] day of life was estimated according to the formula:

$$\text{daily intake / kg bw} = c * 60 / 1000$$

where c is concentration of the chemical per liter of colostrum.

Estimated daily intake of pesticide residues, total (ng/d) according the previous formula and by an average 3.5 kg newborn ($ng/kg\,bw/d$), collected in 2006, was compared with estimated daily intake via colostrum collected in 2003, in the same area and under the same circumstances, which is showed in Table 2.

Table 2. Estimated average daily intake (total ng/d and $ng/kg\,bw/d$) of pesticide residues on the 3[th] day of life

Chemicals measured	Year of colostrums collection (number of samples)			
	2006 (n=22)		2003 (n=18)	
	ng/d	$ng/kg\,bw/d$	ng/d	$ng/kg\,bw/d$
Aldrin	0.07	0.23	n.m.	n.m.
Endrin	0.08	0.28	n.m.	n.m.
Endosulfan I	0.004	0.01	n.m.	n.m.
4,4-DDD	0.05	0.19	n.m.	n.m.
4,4-DDT	**0.08**	**0.27**	**0.2**	**0.06**
4,4-DDE	**0.04**	**0.15**	**1.6**	**0.5**
Endolulfan sulfate	0.01	0.05	n.m.	n.m.
Dieldrin	0.003	0.009	n.m.	n.m.
Endrinaldechyde	0.009	0.03	n.m.	n.m.
Heptachlor	0.04	0.14	n.m.	n.m.
Endosulfam II	0.01	0.03	n.m.	n.m.
α-HCH	0.006	0.02	n.d.	n.d.
β-HCH	n.d.	n.d.	n.d.	n.d.
γ-HCH	n.d.	n.d.	0.14	0.04

n.d. – not detected, n.m. – not measured

Discussion

Concentrations of measured OCPs (DDT and metabolites, HCH and isomers) in 2006 were compared with concentrations of the same chemicals measured in 2003 in the same region (Vukavic et al., 2003) via estimated daily intake. No ecological accident occurred in this region at the time of pregnancy of these mothers or earlier.

The fall of DDE estimated intake was observed, while DDT estimated intake increased significantly. α-HCH estimated intake increased, but β- and γ – HCH was below the level of detection. All other pesticide chemicals were for the first time measured in colostrum in Vojvodina region.

Since biotransformation and metabolism of DDT are slow processes, its significantly higher concentrations in 2006 colostrum, imply the negative DDT balance in examine milk samples which points out recent input of DDT in environment. The most lipophilic character of DDE causes the more stores of DDE in human being than other DDT metabolites, hence, the rise of DDE is expected in future, as the consequence of this recent DDT environmental influx.

Conclusions

Last measurements of OCPs (4,4-DDT, 4,4-DDD, 4,4-DDE, aldrin, endrin, endosulfan I, endolulfan sulfate, dieldrin, endrinaldechyde, heptachlor, endosulfan II and α-, β-, γ - HCH) in 22 samples of 3rd day human colostrum were performed in 2006, using GC-ECD (HP 5890) supplied with a Quadrex fused silica column 5% Ph for OCPs.

DDT and metabolites in 3rd day colostrum were monitored in South Bačka since 1982. DDE, as an indicator of recent influx of total DDT in the environment, continued its significant fall, while DDT increased significantly for no known reason. α-HCH estimated intake increased, but β- and γ – HCH was below the level of detection. All other pesticide chemicals were for the first time measured in colostrum in Vojvodina region. Human milk, was once again a mirror of environmental pollution.

Acknowledgements

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Section 6: Remediation of contaminated sites

REMEDIATION AND SECURING ACTIVITIES AT A FORMER HCH AND 2,4,5-T PRODUCTION SITE IN GERMANY

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Introduction

During the production of chlorinated organics, waste is generated in considerable amounts often contaminated with PCDD/PCDF and other unintentionally produced POPs (Weber et al 2008). The production of Lindane (gamma-HCH) is a prime example. Approximately 85% waste isomers are formed during the production of Lindane (Vijgen 2006). It was common practice to separate the active gamma-isomer and then to dump the remaining 85 to 90% waste material, consisting mainly of alpha-HCH and some beta/delta/epsilon-HCH. In some factories the waste HCH isomers were recycled to produce other products such as chlorobenzenes (Jürgen and Roth 1989, Weber et al 2006). This recycling approach was invented at a HCH production in Hamburg in the 1950th, which commenced Lindane production in 1951 and stored the waste isomers on site for the first three years. The recycling activities started in 1953 with the production of trichlorobenzene and tetrachlorobenzene which in further reaction steps were used to synthesize 2,4,5-trichlorophenoxyacetic acid ester (2,4,5-T) and 2,5-dichloro-4-bromophenol (Bromophos) as marketable pesticides. The production of 2,4,5-T and the decomposition of HCH resulted in the generation of highly PCDD/PCDF contaminated waste (Degler and Uetzelmann 1984, Jürgens and Roth 1989, Sievers et al 1989, Weber et al 2006, 2008). While 2,3,7,8-TCDD were discovered in this 2,4,5-T production already in 1956 by Sorge (Holmstedt 1981), the high PCDD/PCDF contamination of the HCH decomposer residue were only discovered in 1984 (Jürgens and Roth 1989). The PCDD/PCDF content in the residue of the HCH decomposition finally resulted in the closure of the factory (Jürgens and Roth 1989). Most of the PCDD/PCDF ended up in the waste streams and were deposited on landfills (University Bayreuth 1996, Sievers et al 1989), or were destroyed on an incinerator ship in the open sea.

In addition to products and waste streams, the production halls (in particular walls and reactors) from chemical factories synthesizing dioxin precursors (e.g. 2,4,5-T, 2,4-D or Pentachlorophenol), but also from incinerators or secondary metal plants, can be highly contaminated with PCDD/Fs (Weber et al 2008). This can result in considerable exposure of personnel involved in the demolition and remediation at such sites (Weidenbach et al 1984, Degler & Uentzelmann 1983, Kitamura et al 2000, Takata 2003). This has occurred following accidents in 2,4,5-T and 2,4,5-TCP producing factories. Exposures resulted in chloracne occurring in not only the remediation staff but also in their family members due to PCDD/F transfer via work clothes (Weidenbach et al 1984, Degler & Uentzelmann 1983). Similarly, workers demolishing a highly contaminated incinerator in Nose/Japan showed highly elevated PCDD/F concentration in their blood (up to 806 pg I-TEQ/g fat), although no acute impacts on health were observed (Kitamura et al 2000, Takata 2003). These cases highlight that the demolition of contaminated facilities presents risks to the health and safety of associated workers.

This paper discusses the contamination in soil and groundwater and remediation activities at the former HCH and 2,4,5-T production site in Hamburg including demolition activities/strategies of the contaminated buildings. The case demonstrates that high loads of products and wastes can leak into the soil and ground water at pesticide production sites, and that assessment of contamination in subsurface soil, groundwater and building materials is of key importance.

Results and discussion

Exploration, remediation and containment activities at the production site started at the end of 1984 and were conducted until 1998. Additionally, landfill sites where waste from the production are stored were investigated and were (partly) secured (Goetz 1984, 1985, 1986, University Bayreuth 1995, Sievers and Friesel 1989). The main contamination load was found as deposits on the landfills where production wastes (including at least 378 kg TEQ PCDD/PCDF) were stored from more than three decades operation. The deposition sites are not addressed further in this paper but were partly described in other studies (Goetz 1984, 1985, 1986, University Bayreuth, Sievers et al 1989, Schnittger 2001). In addition to the contaminated waste on the landfills, high contamination loads were in the soil and sub-strata of the production site.

Evaluation of underground of the production site

The production plant was constructed on top of a approximately 6 meter man-made fill of relatively inhomogeneous material (sand, gravel, rubble), above a partly porous impervious clay layer of 0.4 to 4 m. The aquifer is between the impervious clay layer and the micaceous clay layer at a depth between 24 to 30 meter.

In total, 196 drillings were performed on and around the production site with approximately 21,000 single measurements. Details on the measurement strategy applied and some results on single parameters were described by Schlesing (1989). From these drillings 78 were deep drillings of 30 to 60 m, some to the micaceous clay layer,whereas the other drillings reached a depth of approximately 8 meters into the impervious clay layer. 73 drilling were extended to permanent wells including 32 wells outside the production area. The detailed screening revealed high contamination levels of the underground, including in particular HCH, chlorobenzenes, chlorophenols but also PCDD/PCDF.

The total amount of organochlorine chemicals in the underground below the production site was estimated from the measurement program and is listed in table 1. In total approximately 830 t of organohalogens (mainly chlorobenzenes, HCH isomers and chlorophenols - were main products and intermediates) were included in a soil volume of 559000 m^3 on the site. Total PCDD/PCDF contamination in the soil was estimated to 6 kg TEQ (table 1). Some details on contamination levels and distribution in the underground were described by Jürgens and Roth (1989). The highest contamination levels was found in the top three meters, but at some areas high contamination levels were found at the impervious clay layer at 7 m. Furthermore, the chlorinated organics have migrated at some locations down to the micaceous clay layer to a depth of nearly 50 m and formed a Dense Non-Aqueous Phase Liquid (DNAPL). The DNAPL phase contained PCDD/PCDF at a concentration of 1,000,000 ng TEQ/l.

The contamination levels markedly decreased outside the production area (Jürgens and Roth 1989). But the contamination also impacted the aquifer/groundwater with chlorobenzenes (with relatively higher concentrations of the more water solulable monochlorobenzene and dichlorobenzene), chlorophenols and HCHs. This aquifer was utilized by the nearby (1500 m) waterwork Kaltehofe (Jürgen and Roth 1989) and a contamination plume was moving towards the water work by the flow gradient. The water work was closed in 1990 (Umweltgruppe Physik-Geowissenschften 1998).

Table 1: Chlorinated organohalogen compounds in the soil of the production area (total volume 559000 m^3)

Contaminant	Amount of organohalogen in the underground of the production site
Extractable organohalogen (EOX) (calculated to Cl)	663 tons
Trichlorobenzenes	402 tons
Tetrachlorobenzenes	104 tons
Total Chlorobenzenes	551 tons
HCH isomers	262 tons
Chlorophenols	18 tons
2,3,7,8 TCDD	4.8 kg
Total PCDD/PCDF TEQ	6 kg

The contamination on the production site was not the result of specific deposition activities but mainly stem from the spillage of daily routine operation including spills from the production processes, leaks from transportation pipes, storage, loading and de-loading of the chemicals and the interim storage of the HCH waste isomers.
This was concluded from the correlation of contaminants in the soil and the respective locations of the productions. If deposition activities on the site would have mainly resulted in the underground contamination then it could be assumed that rather specific deposition areas on the site would have been used. This was only the case for one hot spot where residues from HCH decomposition process, and associated high PCDD/PCDF levels (with the specific HCH decomposition pattern), were deposited (Schlesing 1989).

Remediation and securing measures
At the start of the remediation planning (1984) and within the first phase (untill 1994) the aim was a thorough clean-up of the highly contaminated soil by excavation and onsite incineration of 25,000 m^3 soil and 10,000 m^3 of the contaminated buildings. Further an in-situ bioremediation in combination with an adsorption approach was planned to degrade and remove target contaminants in the contaminated ground water and deeper soil layers not targeted by the excavation. For the latter approach groundwater was pumped, cleaned over activated carbon and pumped back to the ground water enhanced with oxygen and nutrients to increase the biodegradation of contaminants by microorganisms already present in the groundwater.
However, the onsite incineration approach failed due to corrosion problems and other technical difficulties and was stopped after several months total operation time. Also, the in-situ bioremediation which had shown good degradation performance in laboratory did not show the expected effect in the field and was thus discontinued. In this first remediation phase ,approximately 75 million Euro were spent without significant remediation effect.

Therefore, in a second phase (from 1994 onwards) a new remediation concept for the production site had to be developed. The revised concept consisted mainly of a securing strategy of the site. This included the construction of a cut-off wall (1500 m long, 0.8 m thick, 44000 m^2) during the final phase, which covered the entire production area down to a depth of approx. 46 m, reaching 2 m into the water and solvent/DNAPL proof micaceous clay layer. The containment concept also included an asphalt concrete covering of the entire area after removal of the buildings and remediation of the plume outside the area. To assure that the approx. 830 t of organochlorine contaminants (table 1) do not penetrate through the pores of the securing wall into the groundwater outside the contained area, a pump and treat concept was developed for establishing a pressure gradient for water flow towards the site. Also groundwater from the contamination plume having migrated outside the production area was/is pumped to reduce groundwater contamination and prohibit further migration. The pollutants in the pumped groundwater phases were/are stripped and sent to a hazardous waste incinerator.


Figure 1: Pesticide factory at Hamburg Moorfleet prior to demolition


Figure 2: Area of the pesticide factory during demolition phase of the buildings.

Remediation of the buildings
Sixty-four buildings and chemical facilities on the production site needed to be removed for redevelopment of the area (Figure 1 and 2). The contaminants included PCDD/PCDF unintentionally produced during 2,4,5-T synthesis and HCH recycling activities. Several buildings were also contaminated by PCBs which had been used in paints, sealants and epoxide flooring. A graded remediation strategy was developed depending on the degree of contamination largely depending on the PCDD/PCDF, PCB and asbestos content. The wall plaster in several buildings was contaminated with PCDD/PCDF up to several 100,000 ng TEQ/kg (table 2). In some areas even the bricks were highly contaminated. Highly

contaminated areas and surfaces in the buildings were thoroughly screened and selectively removed before break down. This approach minimized the need to work in highly contaminated areas and therefore reduced risks and exposure of the staff. A graded demolition strategy was applied:

- Highly contaminated production buildings (e.g. old 2,4,5-T production, HCH production, old Lindane and Bromophos production, decomposition of HCH; table 2) were demolished under a full protection housing, or alternatively were only enclosed at the sides with an open top and break down operation were performed under a fine water spray film. The latter approach was found to be a very efficient method for the demolition of contaminated building (Varbelow et al 1998) (Figure 3).
- Buildings with high contamination levels in only some specific areas were selectively demolished with graded protection levels for personnel.
- Buildings with only surface contamination were demolished after removal of contaminated materials (e.g. plaster, epoxide flooring, PCB paints), mainly using high pressure water cleaning with waste water catchment and cleaning.
- Buildings without specific contamination in the concrete where just de-dusted with industrial vacuum cleaners and broken down in a conventional manner.

Table 2: Concentration and pattern of wall plaster in the old 2,4,5-T production building and the HCH decomposer building

	2,4,5-T production (ng/kg)	HCH decomposer building (ng/kg)
2,3,7,8-TetraCDD	151000	20700
Sum TetraCDDs	164000	311000
1,2,3,7,8-PCDD	1930	71200
Sum TetraCDDs	35900	1380000
1,2,3,6,7,8-HxCDD	3190	207000
1,2,3,4,7,8-HxCDD	10500	666000
1,2,3,7,8,9-HxCDD	5950	417000
Sum HxCDDs	94900	6330000
1,2,3,7,8,9-HxCDD	30700	3950000
Sum HpCDDs	54800	6860000
OCDD	122000	20290000
2,3,7,8-TetraCDF	455	74000
Sum TetraCDFs	69000	459000
1,2,3,7,8-PCDF	3370	71600
2,3,4,7,8-PCDF	752	18900
Sum PeCDFs	35500	725000
1,2,3,4,7,8-HxCDF1	3370	341000
,2,3,6,7,8-HxCDF	1120	401000
1,2,3,7,8,9-HxCDF	71.4	31000
2,3,4,6,7,8-HxCDF	391	54900
Sum HxCDFs	24500	2180000
1,2,3,4,6,7,8-HpCDF	11300	1980000
1,2,3,4,7,8,9-HpCDF	662	577000
Sum HpCDFs	17100	4450000
OCDF	13700	7650000
Total I-TEQ	**155 577**	**382 000**

A data sheet was established for each building to record a complete documentation of contaminations, the demolition and the disposal. The disposal pathway depended largely on the PCDD/PCDF, PCB and EOX content. Demolition debris with a high PCDD/PCDF content (> 1000 ng ITE/kg or > 100 mg EOX/kg) and PCB containing flooring and wood and insulation materials were sent to an hazardous waste incinerator. Demolition debris below 1000 ng TEQ/kg and below 100 mg EOX/kg was deposited on the site within the securing measures. The metal parts (e.g. girder, double T-girder), largely contaminated with PCB paints, were recycled in secondary iron industry after removal of the PCB paints.

Figure 3: Housing of the old 2,4,5-T production with open roof (front) and selective demolition of the Bromophos production (back) after decontamination of the building.

A total building volume of 130,000 m^3 with a weight of 27,000 t was removed from the site during deconstruction. The buildings were pre-treated with a range of decontamination techniques before demolition. The majority could then be demolished without specific safety measures. Highly contaminated buildings were pre-treated by de-dusting and a specialised technique for demolition was developed. This did not involve using a complete casing for the buildings but was operated with an open roof and used special techniques to avoid the release of dust and pollutants. This approach minimized the need to work in the contamination zone and therefore reduced risk and personal exposure for the staff. It was determined to be a very efficient method for the demolition of contaminated building.
The cost for demolition of the 64 buildings was approximately 9.5 Million Euro. Additionally, the deposition and incineration/destruction expenses were 4.8 Million Euro. The cost for the analytical screenings during demolition were 1.2 Million Euro including 1548 EOX screenings, 224 PCDD/F analysis, 83 PCB, PCBz, HCH, PxCPh analysis and some other measurements. The total cost of remediation and securing activities only of the production site were approximately 110 million Euro.

Current situation of the production site

In 2008, the 10 years guarantee for the securing wall ended. In a public hearing in May 2009, organised by the environmental agency in Hamburg, it was communicated that the securing wall is still fully operational.
The “pump and treat” activities are currently ongoing and to our knowledge no specific time limit is set. From the estimated 830 t of chlorinated organics in the underground 10 to 30 tons have been pumped and destroyed over the last ~15 years. Therefore the largest share of the contamination is still in the subsoil. The contamination in the plume outside the area has decreased over the years, demonstrating a successful containment up to now. For some of the landfills where production waste is stored monitoring concepts are in place.

Conclusions

A key experience from the pesticide plant in Hamburg is that production residues deposited in the landfills together with on-site spillages on the production area (for HCH, chlorobenzenes, chlorophenols and PCDD/PCDF) posed the highest levels contamination and risk and required the greatest efforts/cost for evaluation, remediation and securing. The demolition of

the contaminated buildings were necessary for the redevelopment of the area but posed a relatively minor threat to the environment (but a risk for demolition staff) and could be managed with special techniques developed for this scheme at reasonable cost. The demolition and decontamination of buildings/facilities accounted for less then 10% of the total remediation/securing costs of the production area.
The case revealed that during the routine operations (e.g. production processes, storage, transport) a considerable amount of chlorinated organics (830 t of HCH, chlorobenzenes and chlorophenols) was spilled into the soil of the production area. The case further revealed that these contaminants including the normally low mobile PCDD/PCDF can migrate through the soil and impervious clay down to a depth of nearly 50 meter. Since these contaminations resulted largely from routine operation it indicates that similar contamination can be expected for other production areas of chlorinated pesticides and organics and that similar investigations are necessary for other production sites.
The experiences gained for the screening, securing and demolition of the production site in Hamburg can be valuable for other pesticide and organohalogen production sites.

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MULTI-YEAR OBSERVATION OF CONTAMINANTS SPREADING AROUND THE AREA ADJACENT TO REMEDIATED PESTICIDE TOMB IN NIEDZWIADY

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Summary

Tombs (Mogilniki) are underground places of storage for expired, unwanted pesticides, which contaminate the environment with pesticides used in the 60s and 70s, including POPs (Persistent Organic Pollutants) pesticides. They can be called local „hot spots". The first underground tomb containing obsolete pesticides was removed in Poland in 1996. The tomb was located in the village of Niedzwiady, province Wielkopolskie. During the removal process, about 60 tons of waste pesticides and close to 1500 tons of contaminated soil and rubble were excavated. Tests performed on soil and underground water samples taken during the remediation indicated significant contamination of adjacent areas.

In 1998, following a study of hydrogeological conditions around the site, 5 piezometers were installed in locations where the concentration of contaminants was found to be the highest and also along the direction of the underground water flow. Regularly sampled water was initially tested for the presence of residues of 22 active substances and currently increased to over 40 a.s. found in pesticides. Over the years, adjustment were made in both the scope of measurements and the piezometer and sampling network.

Multi-year observation of the results does not indicate a tendency toward either disappearance or migration of contaminants. Geological studies of the site show that the ground structure is diverse and the arrangement of impervious layers is very hard to determine with high degree of certainty. Complicated geological structure of the site combined with physical and chemical processes taking place a few meters underground make it impossible to conclusively interpret the results.

Because of that, in 2009 additional drill holes were bored and more underground water samples were taken. The testing helped to define the geological structure of part of the site with the highest concentration of contaminants, helped to determine the range of contamination and the direction of contaminants migration.

The paper presents the results of the multi-year monitoring as well as the results of the hydrogeological studies.

Key words:

tomb, piezometers, contaminants, underground water, pesticide waste, remediation, POPs

Introduction

Removal of tombs in Poland started in mid 90s. Systematic removal of such sites allowed to close around 70% of this type of storage places. It is estimated that there is still about 120 tombs, containing around 5-7 thousand tons of waste. Over the years, a removal methodology has been developed, starting with inventorying the amounts of waste, through tendering out to contractors performing the cleanup project, tomb closure and waste removal, to site reclamation.

Tombs constructed in the 70s and 80s of last century were often located without prior site assessment as to their risk for underground water and their technically poor condition (even at the time of construction) did not guarantee any tightness of the structures. Leaking tombs have been a constant, active source of pesticides and other substances discharged into the soil

and water (a peculiar type of a hot-spot). The contaminants were then carried through underground waters, oftentimes far away from their source, thus causing considerable contamination of adjacent areas. Remediation of such large areas of polluted land is difficult and often economically unjustifiable, this is why it is so important to have information on the contaminants possible paths of migration, dissipation and concentration, which involves close monitoring of the extent and level of contamination at the sites that underwent remediation.
Chemical processes taking place underground, combined with a set of hydrogeological conditions specific to each location require an individualized, site-by-site approach. It is necessary to accurately assess the geological structure and hydrogeological conditions of each site, establish a network of piezometers and regularly take and analyze samples of underground water. Such assessments and sample analysis are included in the government program, approved for five years (2006-2010) and realized by the Plant Protection Institute – National Research Institute: Protection of humans, animals and the environment against the adverse effects of pesticide use, including food safety control, task entitled: Monitoring of hazards around pesticide storage sites.

Materials and methods

Back in 1996, Plant Protection Institute closed the first pesticide tomb in Poland, located in Niedzwiady, province of Wielkopolskie. At that time, Poland did not have a hazardous waste incinerator and national laws did not allow waste to be transported abroad, therefore a decision was taken to excavate and repack the waste, and then place them in a newly constructed, safe, interim storage facility. A total of 66 tons of waste and 1500 tons of contaminated soil were excavated. The contents of the tomb were sorted out and repacked into tight steel drums, then put into the tightly welded chamber at the facility (Tank A); the rubble from the well and concrete rings of the tomb, as well as the most contaminated soil dug out from its direct surroundings were stored in the open chamber (Tank B). The facility also has a retention-evaporation pond (Tank C) designed to collect water leaching out of soil stored in Tank B. Effluents from the new facility were directed to leak-proof Tank C, and the area was additionally monitored through a network of wells. The waste was supposed to be stored at the facility until Poland had some technical capabilities for their disposal. The construction of the new facility, training and equipment for workers involved in repacking of waste was possible through funds under the PHARE program. Remediation of the tomb in Niedzwiady was a testing ground for developing the procedures for excavating, sorting, repacking, reclamation and monitoring of the site after tomb closure.
In 2007, all waste secured in drums were finally removed from the Niedzwiady site. The removal of contaminated soil, effluents and closing up the entire infrastructure at the facility is planned for end of 2009 year.
Geological work and site monitoring have already started when the tomb was being removed. Further activities were performed in three stages in 1998, 2008 and 2009.
During the process of transferring the waste into the new facility and then during ground work involving the removal of the most contaminated soil from underneath the concrete rings, samples of soil were collected for analysis.
A total of 100 soil and water samples were analyzed with ~ 2000 determinations of individual active substances. At the same time analyses involved archival materials on the geological structure and hydrogeological conditions, the site was also surveyed.
The terrain around the site is mostly flat, which, combined with pervious formations right beneath the top soil layer favors infiltration of the precipitation water. The formations are about 10 m thick and the first level of boulder clay is about 30 m thick. The area has two

water bearing levels, however only the first one is at risk for contamination from the tomb, therefore it was part of the observations.

In 1998, after the contents of the old tomb were removed, the team started geological activities, involving establishing of a research network around the site. A total of 5 piezometers were installed, not further than 70 m away from the location of the tomb: four along the direction of the outflowing underground waters and one at the inflow towards the site. One of them was a multi-level piezometer. The piezometers became permanent measuring points for sampling underground water and they also gave a more accurate picture of strata structure and the depth of underground waters around the site. As soon as the piezometers were installed, the team started collecting water samples from all piezometers and measuring points at the site. Water samples were being taken from a total of 14 measuring points. At the beginning, sampling took place twice a year, then only once a year.

Hydrogelogical modeling was done based on the concentration of contaminants and it showed that the impact range of the tomb in the underground formations (sands and dusts) reaches 300 – 350m. In 2008, a decision was taken to expand the piezometers network. Two additional measuring points were established along the outflowing underground waters, located 125 and 250 m away from the remediated tomb.

In 2009, a decision was taken to investigate water and soil conditions in greater detail, particularly in the light of anomalies found in hydrological structure around the site. There were 13 probings performed at the site, with the initial assumption of probing down to the impervious strata. Individual probes were set according to a grid, with each hole being checked for the level of underground water. Samples were collected for chemical analyses and basic testing of in-situ parameters was also performed.

The site has been monitored through analyzing the water samples since 1998. At any stage of geological work, water and soil samples were collected. The range of active substances was selected based on the type of pesticides used at the time and considering the type of products found in the tomb. Initial water analyses allowed to determine which active substances were present in the tomb in the largest amounts and they were added to the list of pesticide residues analyzed as part of the project. Initially, the samples were tested for the presence of 22 active substances found in pesticides. Over the years, the list was expanded to include 43 active substances.

In order to isolate active substances, the samples were liquid-liquid extracted with dichloromethane. Organic phase extract was enriched to dry residue, which was then diluted in acetone. The extracts were determined for the presence of organochlorine and organophosphate insecticides, nitrophenols, phenoxy acids and triazine herbicides. After these determinations were complete, PFBBr (pentafluorobenzyl bromide) derivatization was applied to determine phenoxy ester herbicides, i.e. 2,4-D, dichlorprop, dicamba, MCPA and mecoprop. Dithiocarbamate fungicides (a.s. maneb, thiram, mancozeb) were determined through different analyses, i.e. following acid hydrolysis, CS_2 was sequestered and then determined using spectrophotometry.

In 2007-2008, the above method was fully validated and the results confirmed that the method has good limits of determination, falling within the range of 0.005-0.5 µg/l. Recoveries from fortified water samples were >70%, with a variation coefficient of < 15%. Extracted pesticide residues were determined using gas chromatography (GC) with electron capture detection (ECD) and nitrogen phosphorus detection (NPD). From 1997-2007 testing was done using Hewlett-Packard 5890 and since 2008, Agilent 6890.

This year, the results obtained from the GC with ECD and NPD were confirmed with GC with quadrupole mass analyzer (GC-MS), i.e. mass detector. The application of GC-MS produced both positive and negative confirmations.

In 2009, DNOC residues in some samples were determined using High Performance Liquid Chromatography (HPLC). Determinations were made with liquid chromatograph Waters 2695, equipped with photodiode array (LC/PDA).

Results and discussion

Studies conducted over the period of 13 years allowed to determine the geological structure of the area directly adjacent to the tomb, as well as explore the range and level of contamination around the site. The table below presents the maximum and minimum concentrations of DNOC, 2,4 D, γ-HCH and MCPA measured at three different measuring points, including the date of measurement and current level of the contaminants.

Active substance	Piezometer IA			Piezometer IB			Piezometer II		
DNOC (μg/l)	max-2007	min-1999	2009	max - 2007	min - 1999	2009	max - 2002	min - 2000	2009
	41091	**0,8**	**504**	**17797**	**5,6**	**1072 0**	**346**	**3,9**	**-**
2,4-D (μg/l)	max-1999	min-2008	2009	max-1999	min-2001	2009	max-2002	min-2007	2009
	9821	**16,8**	**130**	**2202**	**20**	**92**	**3047**	**0,892**	**0**
γ-HCH (μg/l)	max-2007	min-1999	2009	max-2007	min-1998	2009	max-2002	min-1998	2009
	701,2	**1,2**	**53,7**	**318,7**	**4,7**	**163**	**39**	**0,46**	**0,59**
MCPA (μg/l)	max-1999	min-2008	2009	max-1998	min-2001	2009	max-1998	min-2001	2009
	6896	**4,56**	**139**	**2923**	**7,8**	**34,2**	**5217**	**1215**	**0**

Table 1. Testing results (selected).

The figure below shows the location of individual piezometers around the remediated tomb, areas of highest concentration of contaminants and hydrogeological conditions, as determined by the geological studies.

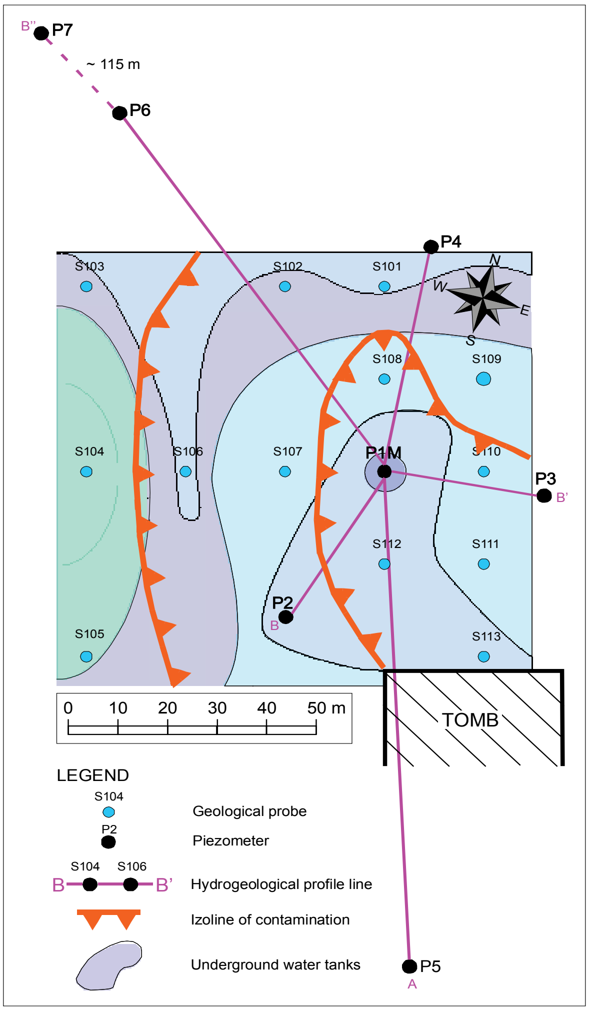

Fig. 1. Hydrological profile lines – piezometers.

The results of the 1998 studies changed what was believed about the underground waters around the site. Big differences were found with respect to the levels of underground water accumulated around the former tomb location, and the distribution of isohypses allowed to think that there was not one but multiple directions of water flow, i.e. water flows radially outward. Observations of contaminant distribution and concentration in each piezometer showed large fluctuation (even within the same year) in the level of contaminants. The area of contaminant accumulation can be clearly seen around the Piezometer P 1M and P2.
These huge concentrations, exceeding several thousands μg/l necessitated expansion of the area under investigation and installation of two additional piezometers along the underground water flow direction. The piezometers installed in 2008, 100 m and 200 m away from the area of highest concentration did not confirm the direction of contaminants migration, which was expected based on hydrological modeling. The results of testing water samples collected from those piezometers did not show the anticipated level of contamination, moreover, the samples were not found to contain active substances.
In 2009, the studies focused on the area directly surrounding the location of the former tomb, which was confirmed to have the highest level of contamination. Geological studies indicate that the sub-surface stratum contains mainly dusty sands and fine sands, interbedded with solid intercalations, like clayey formations. The entire terrain has a bed of boulder clays, whose top is much disturbed and irregular. Water tables appear at various depths within a close distance from each other, which causes formation of a number of small underground

water reservoirs. This type of profile makes individual dens become isolated water reservoirs, filled up after intense infiltration, which discharge water only when the level of ground water accumulation is very high (when the reservoirs overflow). The formation of underground reservoirs causes the contaminants to move as a result of diffusion rather than convective flow, so they become trapped around the tomb and do not migrate freely with the direction of water flow. The results of chemical testing confirmed accumulation of contaminants within a small area and their limited mobility.

Conclusions:

1. Detailed exploration of the hydrogeological conditions around the site is crucial for the right decision as to the remediation of the site and assessing the risk posed by the leftover contaminants.
2. Major contaminants close to the former location of the tomb currently include: DNOC, 2,4-D, γ-HCH and MCPA.
3. Multi-year observations indicate that despite the fact that the Niedzwiady tomb was removed and the area still contains a large load of contaminants, the impact of the site is rather limited and should be considered localized. Despite the fact that the tomb was constructed at a site with unfavorable geological conditions (sands), its impact is limited thanks to a specific structure of impervious strata located deeper in the ground.
4. Very high concentrations of contaminants imply considering additional work at the site to remove the secondary source of contamination, i.e. the contaminated soil leftover after the tomb was removed.

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REMEDIATION OF SOILS IMPACTED BY ORGANOCHLORINE PESTICIDES USING THE DARAMEND TECHNOLOGY

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Abstract

Organochlorine pesticides (OCPs) such as DDT, Toxaphene, and Dieldrin are very persistent in the environment and can pose a threat to human health and other living organisms. They adsorb strongly to soils and do not tend to decompose naturally at a significant rate. Through extensive research and many field projects over the past decade, it has been found that the application of a mixture of solid organic carbon and zero-valent iron (DARAMEND®) to soil and groundwater facilitates the chemical and biological destruction of OCPs. The article provides a description of this approach for treatment of OCP-impacted soils, along with several case studies.

Key Words: DARAMEND, ZVI, pesticide, in-situ soil treatment

Introduction

This article provides a summary of the Adventus Group's experience with treatment of OCPs in soil and groundwater using DARAMEND® bioremediation amendment. DARAMEND is an advanced biological treatment technology for soil, sediment and solid wastes contaminated with recalcitrant organic compounds. When applied to OCPs, the key to this remedial approach is the composition of the DARAMEND soil amendment and application of repeated and sequential anoxic and oxic conditions to the soil matrix. The patented soil amendment is comprised of plant fiber-based organic material and reduced, micro-scale iron (CZ Patent No. 287711). The treatment results in the sequential reductive dechlorination and aerobic biodegradation of chlorinated organic compounds. The amendment is typically applied at low rates (i.e.; <4% w/w) and therefore causes very little, if any, bulking of the soil volume following treatment. Over the last 15 years, the technology has been used successfully for in-situ and ex-situ treatment of soils contaminated with a range of OCPs at sites in North America, South America, and Europe.

DARAMEND For Treatment of OCPs in Soil

DARAMEND is an advanced biological treatment technology for soil, sediment, and solid wastes contaminated with recalcitrant organic compounds. The key components of the DARAMEND technology are: (1) addition of DARAMEND organic amendments to the material to be treated, and (2) regulation of oxygen availability and moisture content by mechanical tillage and irrigation, respectively. The treatment schedule and the formula of the DARAMEND amendments vary depending on the compound to be treated.

For OCPs, an approach with cycled anaerobic and aerobic conditions has been found to be the most effective. For these applications, the DARAMEND soil amendments are composed of organic material (typically 60 to 80 percent by weight), and microscale ZVI (typically 20 to 40 percent by weight). The organic fraction is derived from natural plant fibers rich in cellulose and hemicellulose and, therefore, serves as a carbon source for microbiological consumption. DARAMEND also provides the major, minor, and micro nutrients commonly found in plant material, such as nitrogen, phosphorus, potassium, and trace elements that are required for rapid microbial growth. The amendments are derived from agricultural plant materials and are manufactured regionally to serve international markets (including Australia, Canada, Europe, and the United States) using a proprietary and nonhazardous process.

DARAMEND bioremediation enhances and promotes natural bioremediation rates by adjusting conditions in a soil matrix to stimulate biodegradation of target compounds by indigenous microorganisms. The process is applied in cycles, wherein the contaminant concentrations decrease with each cycle and the number of cycles required to reach the treatment goals depends on the initial concentrations, the responsiveness of the soil to treatment, the amendment application rate, and other factors. Each cycle consists of creating a five-to-ten-day reductive phase followed by a one-to-two-day aerobic phase. The reductive phase involves incorporation of the DARAMEND soil amendment, tillage, and irrigation to approximately 90 percent of the soil's water-holding capacity. Once irrigation is completed, the soil redox potential drops rapidly, and generally reaches Eh levels between −400 and −500 mV. The drop in redox potential is a result of the combined effects of iron oxidation (i.e., Fe^0 to Fe^{2+} and Fe^{3+}) and microbial oxygen consumption. Soil remains in the low Eh phase of a given treatment cycle for between five and ten days to allow time for reductive dechlorination reactions. The treatment cycle is completed with a one-to-two-day aerobic period that is created through introduction of atmospheric oxygen via soil mixing to attain Eh levels of typically +100 to +200 mV. No microbial inoculation is conducted.

Installation Methods

DARAMEND has frequently been applied to excavated soil and dredged sediment in on-site biotreatment cells. The DARAMEND technology can be applied to excavated soil in a number of different formats, including windrows and biopiles, as well as in biotreatment cells. DARAMEND bioremediation can also be effectively applied *in situ* as a land treatment process. Soil and amendments are blended using a rotary tiller, driven by an agricultural tractor, with an effective penetration of two feet. Deeper soil impacts may be treated *in situ* using deep soil mixing equipment or by applying the DARAMEND treatment in lifts. Depending on the cost of excavation and the depth of contamination this may be more cost-effective than *ex situ* treatment. Water content is a critical process parameter and is adjusted using agricultural irrigation equipment.

Soil Treatment Performance

As of this writing, DARAMEND has been successfully applied to more than 4 million tons of soil, sediment, and other materials contaminated with persistent organic compounds, including polynuclear aromatic hydrocarbons (PAHs), pentachlorophenol (PCP), phthalates, chlorinated herbicides and pesticides, organic explosive compounds, and wood preservatives at a variety of industrial and military sites in the United States, Canada, and Europe. As the provider of the treatment technology, given its past effectiveness, Adventus is willing to enter into risk-sharing agreements with environmental consultants and site owners in the form of a remedial performance guarantee. The results from a few recently completed pesticide projects are highlighted in Table 1. More detailed case studies of three applications are provided below. The first two case studies represent *in situ* applications, and the third case study is an example of treatment of excavated soil in an on-site biotreatment cell.

Table 1. Influence of DARAMEND bioremediation on OCPs in soils at sites in Canada and the United States.

Site	Compound	Concentration (mg/kg) Initial	Final	Treatment Period
Uniroyal Chemical, Ontario, Canada	2,4-D	97	3.8	9 months
	2,4,5-T	8.1	1.3	
	DDT	53.5	4.7	
CIBA-Giegy, Ontario, Canada	Metolachlor	72	<1	10 months
	Atrazine	15	<1.5	
W.R. Grace, South Carolina, USA	Toxaphene	239	5.1	4 months
	DDT	89	16.5	
THAN Superfund Site, Alabama, USA	Toxaphene	189	11	10 months
	DDT	84	9	
	DDD	180	52	
	DDE	25	6	
ATOFINA Chemicals Kentucky, USA	a-HCH	7,647	446	99 days
	b-HCH	1,200	373	
	Lindane	567	14	
	d-HCH	747	57	
	HCB	10.9	1.3	
Confidential Client Florida, USA	Dieldrin	0.0459	0.0151	20 days
Confidential Client, Ontario, Canada	DDT	2.05	0.66	3 weeks
	DDE	2.37	0.80	
	Dieldrin	0.110	0.028	

Case Study #1: In Situ Treatment of Dieldrin in Soil

A remedial effort using cycled DARAMEND treatment for removal of Dieldrin from 2,400 tonnes of soil was conducted in November 2004 in coastal Florida. The DARAMEND was applied *in situ* using a deep rotary tiller at an application rate of 0.5 percent DARAMEND on a weight-by-weight basis per cycle. Following completion of two treatment cycles, conducted over a period of two to three weeks, the mean Dieldrin concentration in soil, as determined from six sampling locations, was reduced from 45.9 μg/kg to 15.1 μg/kg (Figure 1). Application of a third treatment cycle resulted in additional removal of Dieldrin to a concentration of 5.8 μg/kg, resulting in a total reduction of between 85 and 90 percent. The remedial objective was met at a total product cost of approximately \$16.30/m^3 soil

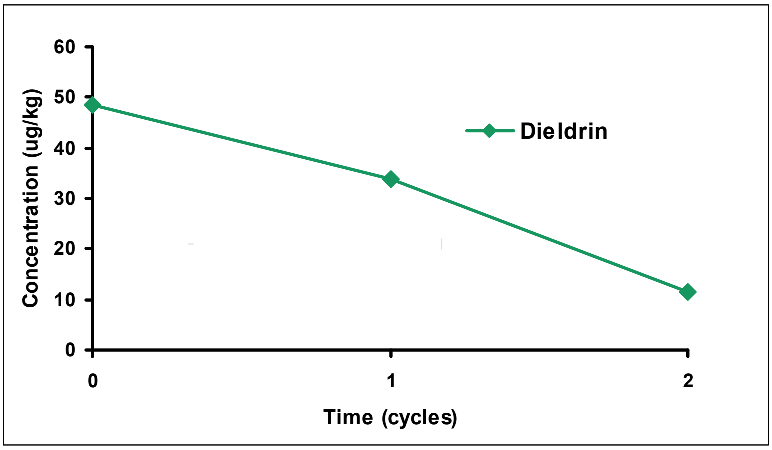

Figure 1. In situ DARAMEND remediation of Dieldrin-impacted soil

Case Study #2: In Situ Treatment of DDT, DDE, and Dieldrin at a Residential Development Site, Ontario, Canada

A residential development was to be built on a former agricultural property, where many decades of application of pesticides to apple trees and strawberry plants resulted in Dieldrin, DDT and DDE residual concentrations in the upper the upper 0.5 m soil that exceeded the standards for residential use.

A successful two-acre (0.8 ha) pilot project was completed in late 2006. By early September 2007, four months after kick-off, the full-scale remediation of an additional 32 acres (13 ha) of soil was completed on time and on budget. The guaranteed fixed-price cost of this turn-key project was less than US$35,000 per acre (less than $23 per tonne). Compared to a theoretical cost of dig and dump of *ca*. $100/tonne, the savings on the project would be over $87/tonne. The Adventus approach resulted in savings of over $4 million compared to the dig and dump estimate.

The DARAMEND amendment was spread onto the soil and incorporated using specialized rotary tillers. Once incorporated into the soil, water was added to achieve the desired moisture content. At this site, only one or two reductive-aerobic treatment cycles were required to achieve the site remediation targets. The results of the treatment are summarized in Table 1. For regions of the site that were treated in one cycle, the average percentage removal ranged from 38% to 53%. For regions that required two treatment cycles, the average percentage removal was between 65% and 68%. Although DDD did not exceed the remedial standards, it was reduced by an average of 57% in one treatment cycle.

Case Study #3: Ex Situ Treatment of Toxaphene and DDT in Soil

Bioremediation of pesticide-impacted soil/sediment was required at a Superfund site in Alabama. Prior to treatment, Toxaphene, DDT, and DDD exceeded remedial objectives in most areas of the site. Toxaphene and DDD concentrations, in particular, were highly elevated in some areas. Repeated applications of DARAMEND were employed to generate sequential anoxic and oxic conditions in the soil. Amendments were incorporated to a depth of two feet using a specialized deep rotary tiller. Water was then applied to bring the soil moisture content up to 90 percent of the soil water-holding capacity. These steps were repeated for each treatment cycle. The amendment dosage was 2.2 percent for the first cycle and 0.7 percent for subsequent cycles, as needed.

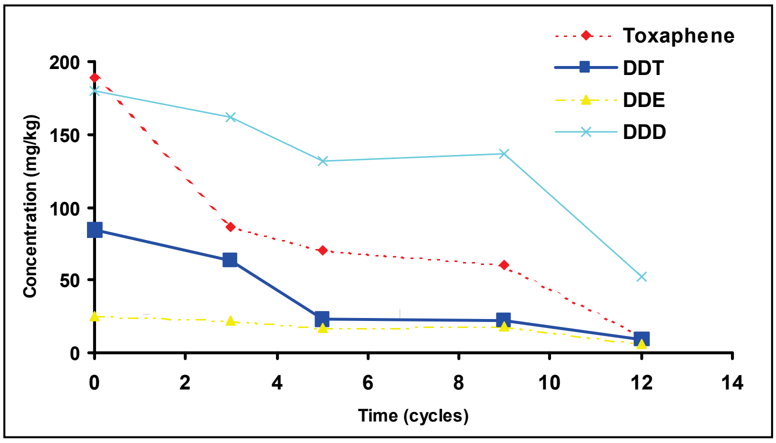

Figure 2. Influence of DARAMEND bioremediation on Toxaphene, DDT, DDE, and DDD soil concentrations

The remedial goals (i.e., Toxaphene: 29 mg/kg, DDT: 94 mg/kg, DDD: 132 mg/kg, and DDE: 94 mg/kg) were reached in all areas of the treatment cell following the application of 3 to 12 treatment cycles (Figure 2). The number of treatment cycles required to reach the remedial goal was primarily dependent on the initial concentrations. Analytical results indicated that mean Toxaphene, DDT, DDD, and DDE concentrations were reduced from 189 mg/kg, 81 mg/kg, 180 mg/kg, and 25 mg/kg to 10 mg/kg, 9 mg/kg, 52 mg/kg, and 6 mg/kg, respectively (Figure 2). This corresponds to removal and destruction efficiencies (RDEs) of 95, 89, 71, and 76 percent. In some sampling zones, the initial pesticide concentrations were much higher than the mean concentrations, and performance in these zones was correspondingly more effective. For example, Toxaphene, DDT, DDD, and DDE concentrations were reduced from 720 mg/kg, 227 mg/kg, 590 mg/kg, and 65 mg/kg to 10.5 mg/kg, 15 mg/kg, 87 mg/kg, and 8.6 mg/kg, respectively, in the more heavily impacted regions of the site. This corresponds to RDEs of 99, 94, 85, and 87 percent.

The treatment cost per ton varied according to the initial concentration and ranged between U.S. $32/ton and $69/ton. The average unit cost for the treatment of approximately 4,100 tons of soils was approximately $60/ton.

As indicated above, variable contaminant concentrations resulted in variable treatment time requirements. Remedial goals were reached after three treatment cycles (six weeks) in less heavily impacted regions on the site, while the most heavily impacted areas required 12 treatment cycles (24 weeks). On average, the remedial goals were achieved following the application of approximately 8 treatment cycles (16 weeks).

SUMMARY

The combination of chemical dehalogenation mechanisms provided by ZVI, with the enzymatic dehalogenation mechanisms enabled when bacteria are provided with a suitable carbon source, results in a robust, multimechanism treatment approach for soil contaminated with chlorinated compounds. This combined chemical/biological treatment method has been widely and successfully applied to soil and groundwater environments using the unique iron/carbon product DARAMEND. In addition, the treatment method is very environmentally sound. The soil can be treated on site as opposed to using landfill space. The process uses little energy and very few resources. Following the completion of treatment the soil can be used for a variety of beneficial purposes. Finally, contaminants are destroyed, not just transported for storage or treatment elsewhere.

BIODEGRADATION OF LINDANE (γ-HEXACHLOROCYCLOHEXANE) AND OTHER CHLOROCYCLOHEXANES USING DARAMEND® TECHNOLOGY

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Abstract
This work was focused on validating biodegradation efficiency of the DARAMEND® *in situ* chemical reduction (ISCR) technology to treat soil highly contaminated by hexachlorocyclohexanes, mainly by the gamma isomer (Lindane). The soil originated in a former Lindane-manufacturing plant in Skopje, Macedonia.
A biodegradation test was carried out in a laboratory scale for almost 6 months. A total of nine sequential anaerobic/aerobic cycles were completed over this period of time. The results showed that the DARAMEND® technology was effective at treating soil containing 36.6 $g.kg^{-1}$ of Lindane and other isomers, α-HCH, β-HCH and δ-HCH at concentrations of 20.8, 1.7 and 25.4 $g.kg^{-1}$, respectively. Total HCH elimination efficiencies of 77% and 85% were achieved when 2% and 4% (w/w) DARAMEND additions were used, respectively. The observed biodegradation rates of HCH isomers varied as follows: γ-HCH > δ-HCH > α-HCH > β-HCH. The concentrations of degradation intermediates were also monitored; the main transient intermediates were chlorobenzene and dichlorobenzenes.

Key words
ISCR, *in-situ* chemical reduction, Lindane, hexachlorocyclohexane

Introduction
Γ-hexachlorocyclohexane (γ-HCH), also known as Lindane, has been used worldwide since the 1940s in agriculture as an insecticide. Although it has been banned or restricted in many countries because of its toxicity and recalcitrant nature, numerous sites still remain contaminated throughout the world and new sites are being generated because of its continued use in some countries.
Commercial formulations of Lindane contain a mixture of additional HCH isomers, mainly α, β and δ. These compounds,are relatively stable and insoluble in water which makes them persistent pollutants. However, several published reports have indicated that those compounds are amenable to bioremediation (Datta et al., 2000; Philips et al., 2004; 2005; Siddique et al., 2002).
In this work remediation of HCH isomers in contaminated soil was evaluated under cycled anaerobic/aerobic conditions. The soil was supplemented with the DARAMEND product (2% and 4% w/w) that combines strong reducing effects of zero valent iron and an organic carbon substrate. Zero valent iron and carbon enhance reductive dechlorination of HCHs in the anaerobic phase and subsequent aerobic conditions allow degradation of metabolic intermediates with organic carbon as a co-substrate.

Materials and Methods

Contaminated soil was air-dried at ambient temperature and homogenized. Baseline analyses were carried out to determine concentrations of HCH isomers and potential intermediate products (benzene and chlorobenzenes). The test was carried out in glass jars filled with 300 g of contaminated soil. A test control (soil without DARAMEND addition) and reactive batches with soil amended by DARAMEND (2% and 4% w/w) were prepared. Duplicate jars for each batch were set up and results are shown as averages (Table 1). Distilled water was added, lids were placed on the jars and they were incubated at room temperature in the dark. The anaerobic phase lasted 10 days then the soil was stirred to initiate the aerobic phase and jars were left with the lids off for the next 4 days. After that samples were taken for HCH isomer and intermediate analyses and the second anaerobic/aerobic cycle was initiated by adding DARAMEND.

Table 1: Summary of treatments with DARAMEND.

Jar	Variant	DARAMEND Application Rate (% w/w)								
		Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6	Cycle 7	Cycle 8	Cycle 9
1, 2	**Control**	0	0	0	0	0	0	0	0	0
3, 4	**2%**	2	1	2	2	2	2	2	2	2
5, 6	**4%**	4	2	4	4	4	4	4	4	4

Results and Discussion

Figures 1 and 2 show the results of HCH degradation in contaminated soil. After 170 days the concentration of the total HCH isomers decreased from 84.5 $g.kg^{-1}$ to 36.5, 19.8 and 12.8 $g.kg^{-1}$ in the control, the 2% batch and 4% batch, respectively. The highest removal efficiency was achieved in the batch containing 4% of DARAMEND (85%), 77% of HCHs were degraded in the batch with 2% DARAMEND and a decrease of 57% was observed in the control. Biodegradation rates of HCH isomers were found as follows: γ-HCH > δ-HCH > α-HCH > β-HCH (in batches with DARAMEND addition).

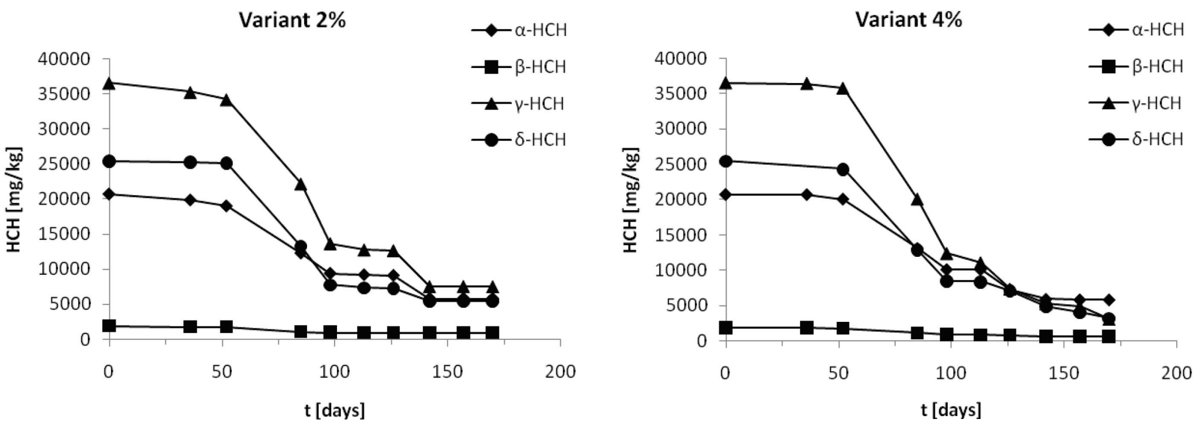

Figure 1: Changes in the HCH isomers concentration in treated soil during the test. Left – batch with 2% DARAMEND addition, right – batch with 4% DARAMEND addition.

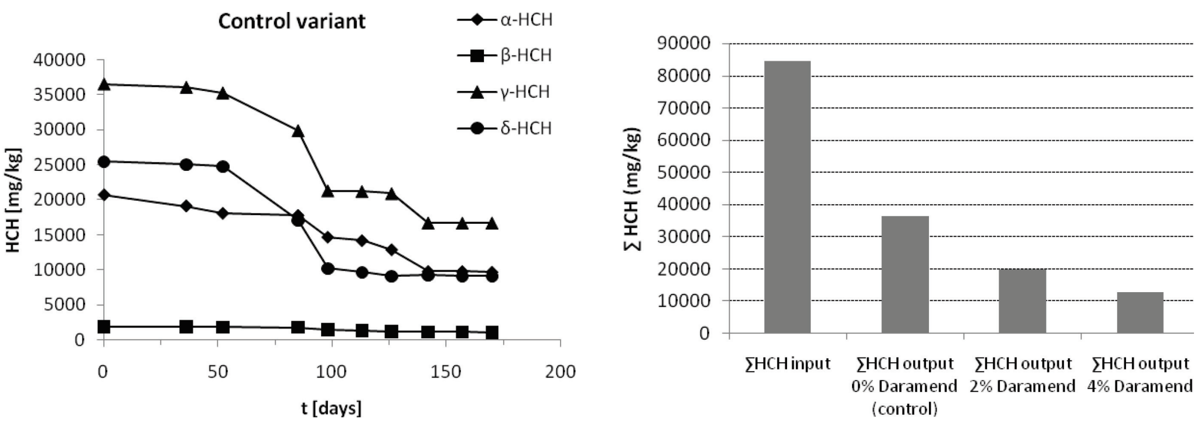

Figure 2: Left - changes in the HCH isomers concentration in treated soil in the control during laboratory test. Right – The total HCH isomers concentration (input and output analysis).

Potential intermediate products of HCHs were also monitored during the bioremediation process. Generation of of benzene and chlorobenzenes was observed (Figure 3). The main intermediates formed in the DARAMEND batches were chlorobenzene and dichlorobenzenes, along with higherchlorobenzenes and benzene. Based on the obtained results, about 18% (molar) of the initial soil HCHs mass was converted to those intermediates. The subsequent degradation of these intermediate products will need to be addressed Decreasing trends observed at the end of the test indicate that degradation of these intermediate products could be achieved by extending the treatment time.

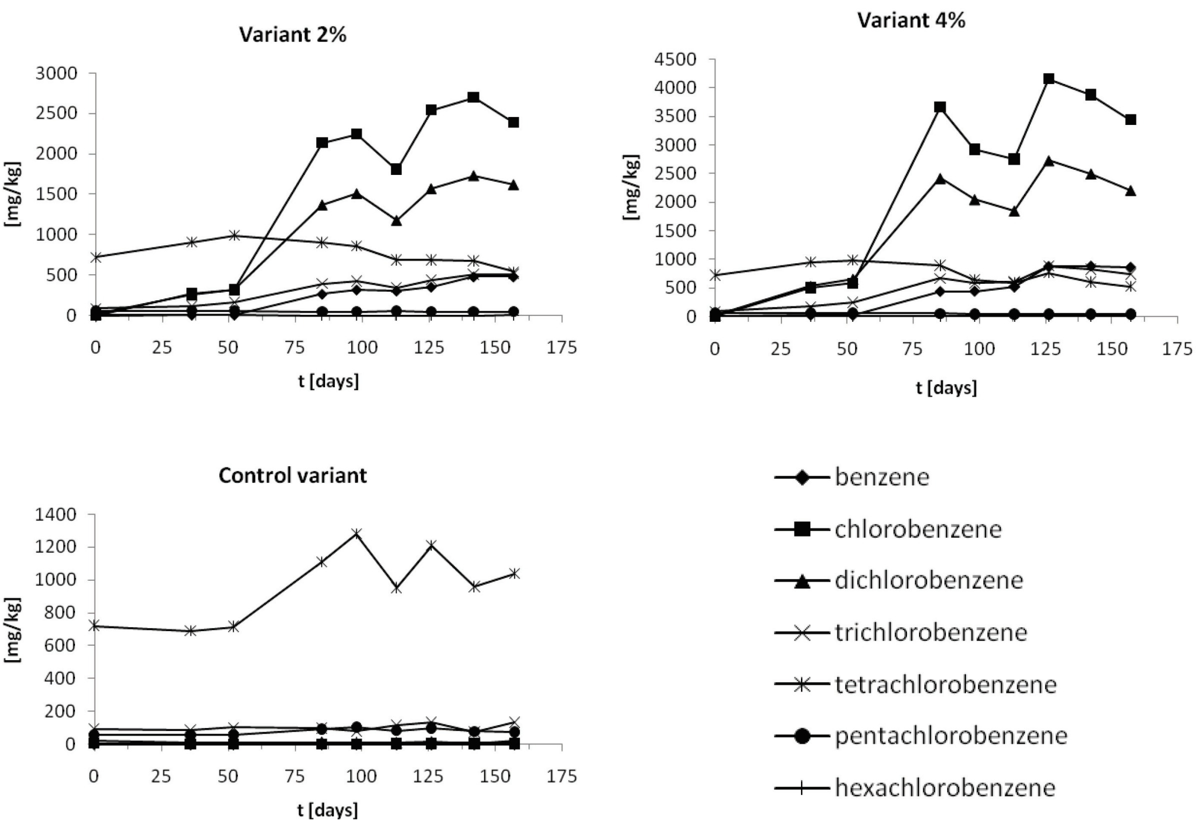

Figure 3: Changes in benzene and chlorobenzenes concentrations in treated soil during model test in variant 2% DARAMEND (upper picture left), variant 4% DARAMEND (upper picture right) and control (lower picture).

Conclusion

Results from the laboratory experiment show that the DARAMEND® *in situ* chemical reduction (ISCR) technology is applicable for treatment of soil contaminated by high levels of hexachlorocyclohexanes. During the treatment, a small fraction of the HCH compounds was transferred to chlorobenzenes and benzene. Degradation of those intermediates in the treated soil needs to be addressed if the technology is used in practice. Results from this test indicate that extending the treatment period could result in a more complete treatment.

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IN-SITU REMEDIATION OF TOP SOIL CONTAMINATED WITH DDT, LINDANE (HCH) AND HEPTACHLOR

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Abstract: Soil contamination with persistent chlorinated pesticides such as DDT, Lindane (HCH-Hexachlorocyclohexane) and Heptachlor can lead to exposure and health risks for local inhabitants due to either direct contact with the top soil, or spreading of contaminated soil dust by wind erosion or in surface runoff.

Around former rural pesticide warehouses, diffuse soil pollution due to activities associated with storage and supply activities is often present in concentrations exceeding soil quality criteria. Since chlorinated pesticides bind strongly to humus in organic soils, the highest soil pollution levels are generally found in the top 25-30 cm of soil. A demonstration project is in progress to evaluate the feasibility of in-situ bioremediation by land farming with addition of amendments - The DARAMEND® process by ADVENTUS. Sequential cycles of anaerobic (no oxygen, strongly reducing conditions) and aerobic (oxygen present) conditions enhance the degradation of chlorinated organics and are generated by mechanical tillage and application of DARAMEND® granulate followed by irrigation to regulate of oxygen availability and moisture content. Between 5 and 10 cycles of treatment are expected to be necessary to treat the top soil at the demonstration site.

Soil contamination often demonstrates spatial heterogeneity that varies over several ranges within short distances and to document the treatment, a sampling and analytical program based on statistical tests is used. The demonstration area of 385 m² including the control area has an average concentration of total DDT, HCH and Heptachlor of 13.9, 23.3 and 5.2 mg/kg respectively. Appreciable heterogeneity is observed and the concentration of HCH ranges from 0.19 to 95.4 mg/kg. The results after 5 cycles of treatment demonstrate appreciable reduction of up to 57% for sum of DDT, 41% for sum of HCH and 73% of Heptachlor.

Keywords: POP, DDT, HCH, Lindane, Heptachlor, bioremediation, land farming, contaminant heterogeneity.

Introduction

Problems with stockpiled Persistent Organic Pollutants (POP's) especially the Obsolete Pesticides (OP) pose a serious risk to human health in the areas where they previously have been stored and used, since most of the POP's are highly toxic even in very small concentrations.

During the last decade, pollution due to POP pesticides has been recognized by the Moldovan authorities as a problem of national priority which needs to be resolved in order to reduce the impact of POPs on human health and the environment. This project for the remediation of POP Pesticides polluted areas is part of project undertaken by Ministry of Ecology and Natural Resources of the Republic of Moldova (MENR) on the "Remediation of POPs Pesticides Polluted Areas and Clean-Up of PCB Contaminated Oil in Power Equipment".

Objective

The objective of this project is to identify cost-efficient remediation technologies for POP pesticides polluted areas and prepare guidelines for the remediation of POP polluted sites in Moldova /2/. Remediation techniques need to be tailored to best fit local characteristics like soil type, hydrogeology, contamination degree, and pesticide category. This paper concerns in-situ bioremediation in progress at one demonstration site.

Method

Site investigation

During the preliminary (2007) and supplementary site investigations (2008), soil contamination with DDT (mainly DDE isomer), HCH (mainly β-HCH isomer) and Heptachlor was found at the site close to a former pesticide storage warehouse. The highest concentrations were 366 mg/kg DW for sum of DDT and 25 mg/kg DW for sum of HCH. Contaminated building rubble from the former warehouse and a sharp pesticide smell were also present at the site, see figure 1.

Figure 1 Demonstration site for bioremediation

Remediation activities

The contaminated building waste and contaminated soil adjacent to the warehouse have been isolated in an on-site waste deposit with bottom and top protective liners (membrane), and secured by a surrounding protective bank and a top layer of clean soil. The waste is fenced and warning signs are posted.

The remaining contaminated soil is treated by an in-situ bioremediation by land farming with addition of amendments (nutrients, organic material as a microbiological carbon source, and reduced iron - The DARAMEND® process by ADVENTUS) /1/.

The site is divided into 5 treatment areas and a control area, see figure 2. Area 1 - 4 (total area of 335 m^2) and control area (total area of 25 m^2) is expected to have a low level pollution. Area 5 (total area of 25 m^2) is expected to have a higher level of pollution. Sequential cycles of anaerobic (no oxygen, strongly reducing conditions) and aerobic (oxygen present) conditions enhance the degradation of chlorinated organics and are generated by mechanical tillage and application of DARAMEND® granulate followed by irrigation to regulate of oxygen availability and moisture content /1/. Degradation of up to 30% - 60% of the organics is expected for each treatment cycle. Between 5 and 10 cycles of treatment are expected to be necessary to treat the top soil at the demonstration site. The treatment can easily be applied by local staff after training.

The vegetation is removed and the soil tilled to break up the soil structure in all five test areas. The soil is also tilled in the control area. Soil samples to establish the baseline level of pollution are taken as described in the statistical design below. The Daramend granulate is distributed at load of about 0.5% wt/wt for each treatment cycle in each of the five test areas amounting to about 930 kg /cycle. The soil is then tilled to mix the granulate to a depth of about 30 cm´s in the soil and the soil is thoroughly irrigated to increase the water content to more than 85% in treatment depth of at least 30 cm.

The anaerobic (reductive) phase: The soil is allowed to rest for at least 5 whole days during the anaerobic (reductive) phase. Reducing conditions need to be maintained during this period to induce reductive dechlorination of DDT and HCH. This can be achieved by ensuring that the moisture content is high by covering the wet soil with black plastic sheeting.

The aerobic (oxidative) phase: The soil is tilled again to provide oxygen and then allowed to rest without any covering or addition of water for at least two days during the aerobic phase.

These two phases are repeated for each treatment cycle. Soil sampling is repeated after 5 and 7 cycles of treatment. After five treatment cycles, the analytical results are evaluated. If an area is still polluted, the treatment is continued up to a total of 10 treatment cycles.

Statistical design for sampling
The sampling program is based on the Duplicate Method as described in /3, 4/ and is illustrated in figure 2. Two composite soil samples; a and b (each composed of 5 random soil samples comprising 0.5 - 1 kg from 10-20 cm´s depth), are taken from each area and the control area. For example, figure 2 shows that A2a is a composite sample from Area 2 made from the 5 random samples as shown in red. A2b is also a composite sample from Area 2 made from the 5 random samples as shown in blue. The soil in the composite sample is mixed thoroughly and two samples from each composite sample are analysed for Heptachlor, α-HCH, β-HCH, γ-HCH, 4,4-DDE, 4,4-DDD and 4,4-DDT by GC-MS.

Results
The results of the baseline sampling of composite soil samples after the area was cleared of vegetation and tilled to mix the soil demonstrated different levels of contamination and composition in the five test areas and the control area compared to the results in the original site investigation in 2007 and 2008 as illustrated in table 1. This illustrates the problem of interpreting soil concentrations based on a few soil samples in the initial site investigations.

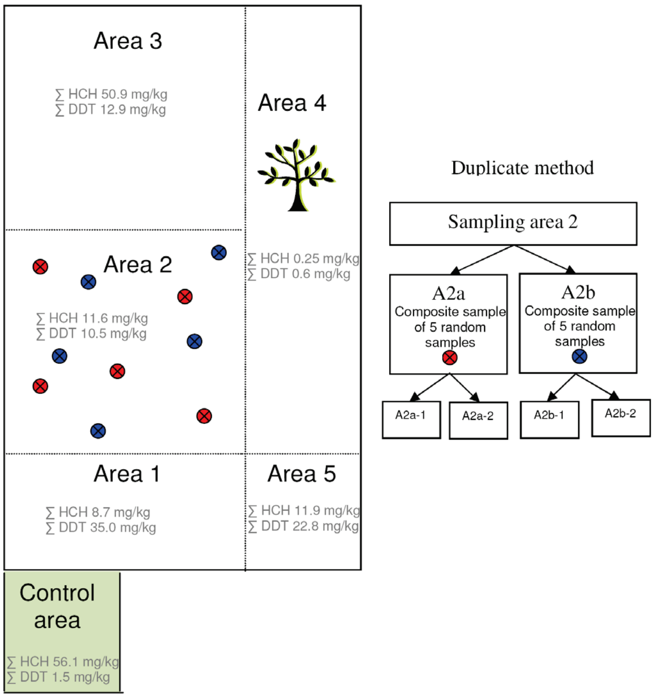

Figure 2 Sampling design to compare baseline concentration with results after treatment

Table 1 Mean concentration in treatment and control area before and after treatment with 5 cycles of Daramend and compared to previous site investigation data.

	Area 1	Area 2	Area 3	Area 4	Area 5	Control area
sum of HCH	mg/kg dw (mean values)					
Site investigation 2007-2008	0.1	0.1-0.2	0.2-0.4	0.2-7.9	0.03-19.4	1.8
Baseline before Daramend treatment	8.7	11.6	50.9	0.25	11.9	56.1
5 cycles Daramend	5.1	8.4	26	0.53	9.4	65.3
% reduction after 5 cycles of Daramend	41%	28%	49%	-	21%	-
sum of DDT	mg/kg dw (mean values)					
Site investigation 2007-2008	1.8	1.8-9.6	0.1-1.3	1.2-9.6	43.6-365	0.03
Baseline before Daramend treatment	35.9	10.5	12.9	0.57	22.8	1.5
5 cycles Daramend	12.7	2.2	5.5	1.3	13.5	0.99
% reduction after 5 cycles of Daramend	65%	79%	57%	-	41%	34%
Heptachlor	mg/kg dw (mean values)					
Baseline before Daramend treatment	3.9	0.50	24.7	0.07	2.2	0.06
5 cycles Daramend	0.49	0.49	4.6	0.35	2.73	0.60
% reduction after 5 cycles of Daramend	87%	2%	81%	-	-	-

As can be seen in table 1, the pesticide distributions are not correlated as the highest concentrations of HCH are seen in the control area and area 3, while the highest concentrations of DDT are seen in area 1 and 5. Heptachlor is found in area 3. However, there is excellent correlation between concentration of p,p-DDE and sum of DDT (r^2=0.9779), where DDE is about 45% of the total sum of DDT. Likewise, there is excellent correlation between β-HCH and sum of HCH (r^2=0.9167), where β-HCH is about 78% of the total sum of HCH. Two samples from area 3 did however have an appreciable content of α-HCH. After 5 cycles of treatment, appreciable reduction of the content of HCH and DDT are seen in areas 1, 2, 3 and 5, and for Heptachlor in area 3. Areas 4 and the control area showed no overall reduction. In both areas, we assess that the overall contamination level is low, but that the results in the composite samples are easily affected by small quantities of soil with a higher contaminant level.

The statistical analysis demonstrated that the sampling uncertainty due to contaminant heterogeneity in the soil is much greater than the uncertainty due to analytical sampling and analysis as illustrated in table 2.

Table 2 Measurement uncertainty and contribution from field sampling and analysis.

	Mean concentration for area 1-5 mg/kg dw	Measurement uncertainty %	Field sampling uncertainty %	Analytical sampling uncertainty %
HCH before treatment	16.7	93	86	36
HCH after 5 cycles of treatment	9.9	70	67	18
DDT before treatment	16.3	95	94	12
DDT after 5 cycles of treatment	7,0	79	76	20
Heptachlor before treatment	6.3	196	166	94
Heptachlor after 5 cycles of treatment	1.7	109	103	36

Conclusions

The in-situ bioremediation by land farming is in progress and the results after 5 cycles of treatment demonstrate appreciable reduction of up to 57% for sum of DDT, 41% for sum of HCH and 73% of Heptachlor. The use of composite samples and the Duplicate Method /3, 4/ has demonstrated a relatively large degree of heterogeneity for the sampling and analytical results for the test and control areas. Using the same sampling design after 5 and 10 cycles of treatment will allow an evaluation of the remediation treatment. The Moldovian soil criterion for pesticides on agricultural land is 0.1 mg/kg for most pesticides (DDT, Lindane, HCH), and therefore the treatment needs to achieve residual soil concentrations around 0.1 mg/kg.

Acknowledgements:

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Section 7: Public Participation-Capacitybuilding

ENVIRONMENTAL (IN)JUSTICE IN BRAZIL: HCH AND OTHER POP CONTAMINATED SITES IN A SOCIAL-ECOLOGICAL POINT OF VIEW

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Abstract
This paper intention is not to be a comprehensive inventory, my aim here is only to describe the tolerance of the whole Brazilian society and especially environmental and health authorities, and how they tried to solve old problems of contamination in my country. Cubatão, Recanto dos Pássaros, Sao Caetano, Cidade dos Meninos. Examples of Environmental injustice, is a way to look to the problem; it affected the workers, the poor and its children by affecting its environment.

Key-words: Brazil, Industrialization, Environmental Pollution, Chlorinated Pesticides, Persistent Organic Pollutants

Introduction
According to the legend, in 1972, during the closure of the First United Nations Conference on Development and the Environment, the Brazilian representative made an "off the records" statement inviting the industrialized countries to invest their money in Brazil. At that time, the Government was ruled by a strong right-wing Military Regime that was promoting a fast economical growth, so called the 'economical miracle' and different efforts to boost the industrial production was under course. The environmental accountability of this progress is still to be completed.

São Paulo: São Paulo is the locomotive of the country. In Cubatão during the 1980's, Rhodia was producing different chlorinated products with minimum care to people and the environment. Thousands of acres of mangroves were affected by illegal dumping of chlorinated waste materials. Until today, more than 15 years after the closure of this factory, workers still suffer with chloracne and different fisheries resources are still contaminated in the most affected areas, like the Samaritá area. Indeed, that time, Cubatão was said to be the most polluted town of the world. The poor people live near the mangroves; they collect crabs in their struggle to survive. What happens to the crabs of the mangrove if there is a non-controlled chemical dumpsite nearby? Cubatão, Samaritá, São Vicente. The former is one of the oldest cities of Brazil. The modern Brazil forgot its past by creating a huge industrial area at one of the most beautiful estuaries of the country. Chemicals were produced, today there are hundreds of people still waiting to for its human rights, some of them still have chloracne, they lost their jobs, and they lost their families (1).

São Caetano do Sul: São Caetano do Sul is one of the oldest industrial sites of the Sao Paulo ABC area. The insecticide BHC (the old term for HCH) and Benzene are two of the 44 dangerous substances that were found in the area. São Caetano do Sul is the cradle of the first Industrial Company of Brazil, the Indústrias Reunidas Matarazzo. The organochlorinated insecticide was one of the main products of the Matarazzo factory that was the owner of this land. From the late 1930 until the end of 1960, different chlorinated pesticides and several other chemical products were formulated in this site that included an oil refinery and a metal smelter. The factory does not exist anymore but some of the old buildings remain as a huge scar in the middle of the town, being crossed nowadays by a suspended road. In spite of the fact that this whole land is still to be cleaned-up, a branch of the University of Sao Paulo was constructed inside the area.

Campinas: More recently, near Campinas, another very important industrial area very close to the Paulinea Oil Refinery, an old industrial area belonging to a pesticide factory of Shell Co. was badly affected by a chronic pesticide spill (Aldrin). The factory was closed in the 1990's. Most of the farmers and settlers living near this area, called "Recanto dos Pássaros", meaning something like "a place for the resting songbirds" had to be out of their lands after the ground water was found highly contaminated by this pesticide. They were partially being reimbursed by the company after a very complicated legal struggle.

DDT in Bahia, Askarel in Rio de Janeiro: At Feira de Santana, an important commercial town Bahia, an old storage site for DDT to be used in Malaria, Leishmaniasis and Chagas disease control was let to rest for more than 10 years inside a very unsafe place, but in this case there was at least a roof over it. However, this was not the case in other places, like the CENTRES, a kind of centre for the treatment of industrial wastes near the main water source of Rio de Janeiro metropolitan area, were Askarel rusted metallic drums were let standing in the rain. This are just few examples, they illustrate quite well the size of problem and the way they have been treated by the authorities from the political sector.

Cidade dos Meninos: Between 1950 and 1962 at a place near Rio de Janeiro called "Cidade dos Meninos", a factory of HCH and DDT for use on vector control operated at the vicinity of an internal school for poor children. In 1955, this school for poor children shared the same area with a factory of HCH. The factory stopped operation letting in place huge amounts of highly chlorinated residues. Thirty years had passed until the police realized that people were selling this residue as a pesticide in at the local street markets. Several testimonies said that blocks of HCH raw material were used to 'pave' the road that crosses this area. Scientists from different Universities had worked in this area; they found contamination of milk, human blood and probably some cases of cancer. Since the closure of the facility, several tones of highly chlorinated residues of this production was let standing at this site without any protection. During more than 30 years, cows and subsistence agriculture flourished in the vicinity of this area. No, its not a joke, creation animals and small agricultural parcels where also part of this neighborhood for THREE DECADES until the authorities rediscovery of the contaminated site in the end of the year 1989. In 1995 after removing up to 40 tones of residues from the site, a secondary attempt to clean the site has augmented the problem: more chlorinated by-products were supposed to be produced "in-situ" after the mixture of the contaminated soil with hydrated lime. It's impressive, that the only answer of the health authorities, the owner of the factory and also partially responsible for the poor children school was to accept that the most contaminated area to be mixed with lime. Engineers from Nortox, a Brazilian Company that proposed the action, said it could solve the problem and would neutralize the pesticide. However, the reactions produced a more widespread contamination (2).

Legal actions: This 'remediation' action occurred in 1995. In 1997, after 7 years of diffuse legal actions the Federal Government was suited and ordered to remove all of the 1.346 person that still live in this area. Since most of the people are very poor, only two families has suited the government on their own and wined the process. In 2004, as a result of this legal measures, the Federal Government send to the Legislative a Project of Law (PL) stating that R$10.000 (US$ 4.500) will be given to each person that agreed to get out of the area (up to R$ 50.000 / family). This amount of money, however, is less than 20% that what is given in average, for those who lost a job or was put in jail during the military governments in Brazil (1964-1985). In time: the PL is still under discussion at the Congress. There are other court decisions in one of this case, one of the oldest social-environmental conflicts of the country, aiming to raise this amount of money up to U$ 50.000 per affected person. Why, after more than 45 years, the Government has now decided that these people have to move out of that land? This year, 2009, a new Federal Commission was formed to deal with the 'Cidade dos Meninos' case. The Government has recognized its responsibility over the 19 km^2 where different contaminated areas are located. But there are families that do not want to go out from that area; they refused to be removed in spite of all of the calculated risks (3).

Refineries, Steelworks, Smelters and Coal Power Plants: Meanwhile, Brazil is investing in two new oil refineries; the one located at Rio de Janeiro State will be the hearth of a new Petrochemical Complex that will use the heavy oil from the mature oilfields of the so called 'Bacia de Campos', a whole enterprise network devoted to plastics. Also, a new Thyssen Steelworks, in a joint venture with China, is being built at the Eastern Portion of Rio de Janeiro Metropolitan Area. Coal will be burnt nearby to generate locally huge amounts of electricity, probably the main power for this new industrial area.

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TWO EFFORTS TO DEVELOP VISUAL AND OTHER TRAINING SUPPORT FOR INTERNATIONAL PESTICIDE CONTAINER MANAGEMENT

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Abstract

A few years ago, the FAO saw the need to develop more uniform guidance on pesticide container stewardship, correctly recognizing container handling challenges to human health but also the creation of a "model" for container stewardship around the globe. This *predominantly text* 2008 ***Guidelines on Management Options for Empty Pesticide Containers*** normalizes the FAO ideals for empty pesticide container stewardship. Implementing this Code of Conduct is now a task before the world community. In some instances, this is not difficult; in other regions of the world it is not as easy. If a significant number of pesticide handlers cannot adequately *read* the FAO Code or any textural training materials then environmental health remains a challenge. For example, of approximately 195 nations, 9 of 10 countries with the highest levels of *illiteracy* are disproportionately located in Equatorial or Central Africa and most of these nations have pesticide stewardship issues.

Understanding any written language ("literacy") is not the only impediment to pesticide safety. In fact, the worldwide ability to read is quite high. One has to look below the ranking of 150 out of 195 nations to reach less than 66.6% literacy levels. *Ethnologue* lists 6,809 living world languages. This suggests that the largest impediment to communication is often *availability of training in a given language* more than illiteracy. The 6 FAO languages are a good start, but only a start.

In 2008, The Pesticide Stewardship Alliance recognized the contribution of the FAO Code of Conduct for pesticide container stewardship and sought solutions: (Phase 1) to better implement the Code through use of visual and train-the-trainer aids, and (Phase 2) address situations where resources for pesticide management are lacking. This effort may depart from strict adherence to the FAO guidance, but not its intent. Progress on both programs will be presented.

Presentation

When organized pesticide container stewardship programs appeared in developed nations more than 25 years ago, pesticide handler training became a necessary companion for improved environmental health and safety. Training materials evolved, usually fitting the resources available to the target audience: their language and their level of sophistication. In relatively rare instances, training was supported by quantities of visual aids, yet the predominant media was textural. Worldwide or even within nations, the instructions were sometimes slightly different or inconsistent. Training based on custom and tradition was as likely as *best practice* education based on verifiable scientific research.

The FAO saw the need to develop more uniform guidance on pesticide container stewardship, correctly recognizing that regularized Code of Conduct would not only serve to protect human and environmental health, but would also create an improved model or direction for pesticide container stewardship programs around the globe. The output from an international panel of experts was published May, 2008 as *Guidelines on Management Options for Empty Pesticide Containers.[1]* This Code of Conduct normalizes the FAO ideals for empty pesticide container management and provides instructions for emptying and handling smaller containers that can be held in hands, larger containers too heavy to be held in hands (drums),

pressure rinsing of smaller containers and larger drums. This document is published in the 6 accepted FAO languages.
Implementing this Code of Conduct is now a task before the world community. In some instances, this is not difficult; in other regions of the world it is perhaps not as easy. Literacy, or inability of anyone handling pesticides to read not only the FAO Code of Conduct but also the product label and any textural training materials remains a challenge in all pesticide stewardship and safety efforts. Political debates vary any listing, but there are approximately 195 recognized nations on the planet.[2] There is, however, less debate on the nations or regions with the highest levels of illiteracy: Afghanistan and some nations in Equatorial, West and Central Africa comprise the states with the lowest levels of *literacy.* [2]

The ability to read and understand any written language is not the only impediment to pesticide safety and container stewardship. In fact the ability to read one or more languages worldwide is quite high. In ordinal ranking, one has to look below the 150 out of 195 listing of nations (lower 23%) to reach the less than 2/3rds level (66.6%) literacy.[2] Statistically then, the larger impediment to effective communication is often more the *choice* of language, as opposed to the *inability to read* and understand *any* language. The international organization, *Ethnologue,* estimates that there are 6,809 living world languages.[3] The challenge for disseminating textural knowledge, including any pesticide management knowledge, sometimes comes down to finding a way to communicate directly to the target audience in way that they can first acquire, then retain as memory. The 6 FAO languages are a good start, but only a start. And yet, no one would suggest that the FAO or any central organization print training materials into thousands of languages.

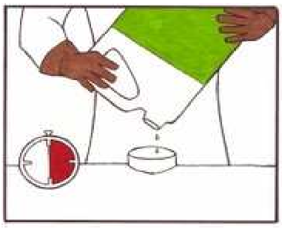
Finally, there is the limitation of words themselves. Arguably, all of us learn in slightly different ways, depending on our culture and experience. Yet, there are only a handful of types of learning and some categories of mental processing predominate. In the world of agricultural and environmental safety training, information transfer, and presumably the transfer of the FAO Code of Conduct, is most frequently attempted through verbal and written instructions. Malcolm Caldwell, author of Blink: The Power of Thinking without Thinking; said, “We learn by example and by direct experience because there are real limits to the adequacy of verbal instructions.” [4] This may be true, especially the assertion that verbal instructions are inadequate, but it also impractical, and possibly dangerous, to learn pesticide safety from experience alone. Visualization, demonstration by a competent expert, and finally, hands-on, adequately supervised practice are shortcuts to “try and fail” life experience and are possibly the most effective pesticide education tools. To achieve this end, the first step toward increased memory cognition, or desirable conduct for handlers of pesticides containers, could be visual images to better imprint any best management practices. According to a recent article in Memory and Cognition: *“The picture superiority effect has been well documented in tests of item recognition and recall.”[5]* Images, better than text, or in addition to text, give our minds a mental experience that is far more indelible.

In 2008, The Pesticide Stewardship Alliance recognized the contribution of the FAO Code of Conduct for pesticide container stewardship and sought solutions to 1) better implement the Code and 2) address, if possible, situations where even the most basic resources for pesticide management and communications were stressed or lacking, and yet dramatically improve the acquisition and retention of fundamental pesticide stewardship principles. The organization, TPSA, is an alliance of regulatory or public sector interests, academia, and private sector-industry concerns. [6] It was founded in North America, although it has grown to encompass stewardship issues and solutions in South America, Asia and Africa. A core group of TPSA active participants have developed pesticide training programs throughout the US and Canada, a relatively well resourced agricultural community. But certain TPSA members are also experienced in more stressed environments, specifically in West Africa. Using their combined backgrounds; The Pesticide Stewardship Alliance chose to simultaneously explore ways to better deliver the pesticide stewardship message. The first project, or Phase I, aims to strengthen the delivery of the FAO Code of Conduct content through visual media that illustrate and make memorable specific residue removal instructions. A second project or, Phase 2, is targeting truly developing countries where resources for both container management and user training are stressed. Here, the project developers are drafting not only the pesticide container stewardship "message," but an adaptive train-the-trainer delivery system. The TPSA International Committee intends to field test this Phase 2 program in an appropriate location: Senegal or Mali.

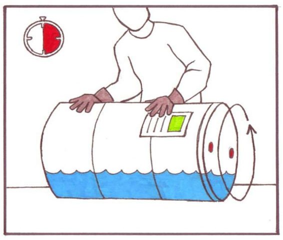
Phase 1: Visual Supplements to "Guidelines on Management Options for Empty Pesticide Containers"

The FAO Code of Conduct is an improvement on most regional, public and private training efforts around the globe. Therefore, this project is not attempting to change the message of this document in any way, but strives to provide a *visual* supplement to a few small, but important sections on residue removal and important points regarding final container disposition. Specifically, the project targets Section 1.5.5 Triple Rinsing for containers small enough to shake *and* for containers that are too large to shake; Section 1.5.6 Pressure Rinsing and select, important messages from following sections on rendering containers unusable and a brief messages regarding final disposition.

The Pesticide Stewardship Alliance's - International Committee has several ideals or goals in mind as they complete this task: 1) the emphasis of the image is on the process, not the artwork or any other aspect of the image, 2) the image should ideally convey and make



memorable each step of the process, 3) the setting of the images are universal and convey no geographical context, 4) in so far as possible, any representation of figures are without prejudice or identification to any religion, race or other ethnic identifications, 5) images work in either color or black-white formats in any media including grouped in a logical sequence on a poster. A train-the-trainer manual will demonstrate how these images may be used in classroom or field training applications.



The inspiration for this sequence owes a debt of gratitude to many prior efforts, especially a number of CropLife efforts around the globe, [7, 8] the ACRC training programs in the US [9, 10] that were also incorporated into the ASABE Container Rinsing Standards [11] and a number of University training programs,[12, 13] especially the illustrations accompanying the Purdue University training on Pesticide Container Management[14]. The design, preparation and critique of this sequence was presented to an audience of experts in Albuquerque, NM; 2009-02-24 and changes were suggested for almost every image[15]. A grant was received in July 2009 to complete this draft "storyboard" and updates are posted: www.tpsalliance.org/

Phase 2: Development of a Training Program for Triple Rinse and Disposal of Pesticide Containers in Developing Countries

Where the Phase 1 project is designed as a training aid to fit into the most universally acceptable, generic setting to assist in implementing a narrow portion of the FAO Code globally; the Phase 2 project is intended as a model of a program that can be used to assist a truly developing region, in this case West Africa. This project targets pesticide container residue removal, but more as a part of a broad spectrum of pesticide safety education and the preparation of not only the message, but also the tools and system for delivering that message. In this effort, development of the total training or content takes into account the availability of basics: gloves, masks, facilities, water sources, ability to manage the volume and fate of rinsate, practical means of preventing exposure in this particular setting, how and where to interact with the intended audience, and preventing environmental contamination in preparation and proper disposal of not only containers, but all related materials. A major emphasis of this project will center on ensuring adequate residue removal from containers, where the small sizes and configurations are almost unique to this region. Another aspect is portraying adequate rinsing and proper container disposal in areas where water resources are an issue and solid waste infrastructure and recycling options usually do not exist. Finally, a major educational effort will attempt to steer the population away from any reuse of pesticide containers, through better understanding of the risks and potential for harm. [16, 17]

Members of TPSA's team have experience in how to put together the tools that provide the best retention of ag. safety training.[18] Shown here, amid various tools in a trainer's kit, are large flip charts containing culturally appropriate images of what to do and what not do for safe handling of pesticides. These are used in field training exercises often held in the middle of the day between work sessions. Also seen in the trainer's tool kit are bottles of dyes or other non-toxic agents that can be used for triple rinse demonstrations practiced on clean unused, but appropriately sized plastic containers. This combination of flip chart visual images as memory cues, then demonstration and finally hands-on student practical experience, will hopefully demonstrate the efficacy of this Phase 2 TPSA project in West Africa and serve as a model for development in other world regions.

Conclusion: The Pesticide Stewardship Alliance welcomes any HCH – Pesticide Forum participant that is interested in reviewing and contributing to either of these projects. For more information contact: rdenny@arrowchase.com and review drafts on TPSA's website.

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INFORMATION AND AWARENESS CAMPAIGN ON POPs IN MOLDOVA

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Abstract

The Awareness, Information and Education Campaign in the field of POPs in the Republic of Moldova is implemented within the GEF/WB Project "Persistent Organic Pollutants Stockpiles Management and Destruction Project" in the period June 2006 – March 2010 at the national and local levels. It is implemented by five teams (organizations) with experience in the field of information, awareness and education, selected through a tender procedure: Association INQUA-Moldova, the Regional Environmental Centre for Moldova (REC Moldova), Moldovan Ecological Movement (MEM), Garamond Studio SRL and Casa Imago SRL. The Objectives of the Campaign are oriented towards:

– conducting an information, awareness and education campaign in the field of POPs in Moldova and organization of conferences and workshops at the international, national and local level;

– developing and carrying out an educational process for the target groups with higher exposure for POPs impact (women, children, farmers, employees of the energy sector etc);

– providing assistance to the Ministry of Ecology and Natural Resources (MENR) in the strengthening of the Environmental Information Centre (CIM) in the field of POPs information.

In the period of 2006-2009 the following major results of the campaign could be mentioned: organized more than 12 information and training workshops, with more than 1 000 participants, representatives of the local public administration (localities of project implementation), environmental protection institutions, health care organizations, plant protection inspectorate, emergency situations and fire inspections, NGOs, representatives of the beneficiaries and mass-media; conducted two national, one local public opinion survey and target groups surveys in order to evaluate the level of knowledge in the field of POPs; developed posters, leaflets, brochures, calendars; organized TV and Radio programs, press-conferences; organized and carried out the works of the 9th International HCH and Pesticides Forum, for information exchange, presentation of the results of implementation of the Stockholm Convention in the region and in Moldova, facilitation of the dialogue with the potential partners and donors in the region (20-22 September 2007, Chisinau). At the same time there is a national web page www.modlovapops.md where all POPs activities are shown and updated monthly. In order to assist other interested people from Moldova a hotline were established within the Sustainable POPs Management Office.

Key words: Persistent Organic Pollutants (POPs), awareness, information and education campaign, target groups, POPs impact, Environmental Information Centre (CIM).

The Awareness Campaign on POPs in Moldova

The Awareness Campaign on POPs in Moldova was launched in June 2007 at the national and local levels ant it is implemented by five teams (organizations) with experience in the field of information, awareness and education, selected through a tender procedure: Association INQUA-Moldova, the Regional Environmental Centre for Moldova (REC Moldova), Moldovan Ecological Movement (MEM), Garamond Studio SRL and Casa Imago SRL.

In the period of 24 month of implementation (June 2007 – June 2009) within this project component were implemented the following major activities:

Conferences, workshops and trainings:

- Organized 3 Launching Workshops (by zones, Cahul, Balti and Chisinau – June-July 2007) with a total number of 180 participants, representatives of the local public administration (localities of project implementation), environmental protection institutions, health care organizations, plant protection inspectorate, emergency situations and fire inspections, NGOs, representatives of the beneficiaries and mass-media;
- Organized and carried out the 9th International HCH and Pesticides Forum, for information exchange, presentation of the results of implementation of the Stockholm Convention in the region and Moldova, facilitation of the dialogue with the potential donors in the region (20-22 September 2007, Chisinau);
- Established Initiative Groups, composed from representatives of the rayon councils, mayors, NGOs, environmental authorities, plant protection, health care, emergency situations representatives from the rayons, were the project activities took place or were planned. Working meetings were organized and took place in the following 10 rayons: Stefan-Voda, Hincesti, Cimislia, Orhei (Pelivan), Riscani, Floreati, Soldanesti, Briceni, Comrat (Vulcnesti) and Dubasari (Cosnita);
- Organized 6 zonal training workshops for the target groups – separately for women and farmers, in partnership with the National Farmers Federation and the Association of Women for sustainable development and environmental protection (June 2008, Balti, Chisinau, Cahul) and one of the replication workshops (October 2008, Ciobalaccia, Cantemir);
- Organized the Informational workshop for public servants (ministries, departments, agencies) and NGOs on the implementation of the Stockholm Convention and related conventions in the field of chemicals and pesticides (Implementation Guides, reporting obligations – July 2008);
- Organized the National Informational Workshop, December 2, 20008, during which the results of the year were presented and introduced all ongoing or planned projects in the field of chemicals and pesticides in Moldova. Up to 100 participants attended: governmental and non-governmental institutions, main stakeholders, media, representatives of the local public administration (localities of project implementation), environmental protection institutions, health care organizations, plant protection inspectorate, emergency situations and fire inspections, NGOs, representatives of the beneficiaries and mass-media;

- Organized the meeting of the NGOs Network on POPs, with 50 NGO representatives, leaders of key environmental organizations, involved or interested in POPs activities (December 2008);
- Organized the Informational workshop for representatives of the ministries, departments, agencies and NGOs, members of Working Groups of the implementation of the Stockholm Convention and related conventions (Rotterdam, Basel and SAICM) in the field of chemicals and pesticides, to present the draft updated POPs NIP Priorities and activities for 2010-2015 and part of the POPs activities within the SAICM Program and Action Plan, needs for the implementation of the Rotterdam Convention in synergy with the Stockholm Convention requirements and preparation for the COP 4 of the Convention in Geneva (May, 2009).

Public opinion monitoring:

- First national public awareness survey carried out in order to evaluate the level of knowledge in the field of POPs and data proceeded;
- Carried out surveys at the local level and target groups surveys, to evaluate the level of knowledge and understanding of POPs problems at the local level and selected stakeholders;
- Second (repeated) national public awareness survey carried out in order to evaluate the level of knowledge in the field of POPs after 2 years of awareness activities and data proceeded.

Capacity building:

- Evaluated the capacities and needs of the Centre of Environmental Information (CIM) of the Ministry of Ecology and Natural Resources, the level of knowledge of the problem by the center's officers, the level of their involvement in the information and awareness in the field of POPs, identification of the technical level, of the publications in the field, present in the center's library. The CIM was supplied with all publications in the field of POPs, available or published by the moment in Moldova and region, including within the publication sub-component of this campaign.

Publications and information materials:

- Developed and published 2 posters: „Stockholm Convention: a chance for a cleaner environment in Moldova", „Chemical warehouses – danger for health and environment" (1000 and 4000 copies each), distributed broadly in all rayons, to NGOs, schools etc;
- Developed and published 2 leaflets: „POPs Management in Moldova" (English) and the „Chemical warehouses – danger for health and environment" (1000 and 4000 copies each). These publications in the field of storehouses were broadly distributed around the country to main beneficiaries;
- Developed and printed the 2008 and 2009 Calendar with the slogan: "Stockholm Convention: a chance for a cleaner environment in Moldova" (2000 copies);
- Developed and printed the brochures „Women and their toxic world" and „Management of the phytosanitary products: personal security and environmental protection – for the target groups workshops (1000 copies each) and distributed to national libraries, Academy of Science, NGOs etc.;

- Developed and printed the set of information and awareness stickers: „Did not pollute the environment with chemicals!” and „Attention! Persistent Organic Pollutants” (1000 copies) in order to label the contaminated sites and serve as awareness tool;
- Prepared and published articles on POPs and project implementation, impact and awareness in each number of „Natura” magazine (monthly, 6500 copies), in the Information Bulletin of the MERN and in each number of the Information Bulletin of REC Moldova (1000 copies quarterly);
- Developed the concepts and contents for the remained printed materials: brochure and monograph on POPs in Moldova, poster and leaflet on the results of the project implementation to be elaborated and printed in the second part of 2009.

Work with mass-media and project activities promotion:

- Developed and places 4 TV and radio spots, produced 6 radio programs with an informational character on POPs issues (radio „Sanatatea”, „Antena C” and National Radio), developed the scenario and finalized the works for the development of the documentary film about the process of project implementation, packaging and evacuation of the POPs from Moldova;
- More than 30 interviews at radio and 4 TV Programs, including at the programs „Buna dimineata!”, „Buna seara!” and „Bastina” (TV Moldova 1).
- Presentation and promotion of the project activities by an informational stand at the MoldEco International Exhibition 2007 and 2008 (end of October, each year).
- Developed and launched the home page of the project: www.moldovapops.md, established the concept, data base. The training of the project unit on the administration and maintenance of the web site took place. The promotion campaign of the project’s web site took place.
- Organized 5 Press Conferences (launching of the evacuation works, April 2007, launching of the information and awareness campaign, July 2007, pesticides forum, September 2007, results of the year, December 2007 and the launching of the second stage of shipment of POPs pesticides, February 2008. For two press conferences field trips were organized (Ratus, Telenesti and Tudora, Stefan-Voda);
- Developed and promoted the placement of the link to the project web site on the home page of the Ministry of Ecology and Natural Resources (http://www.mediu.gov.md/md/of_proiecte/) providing the link to the home page of the project: www.moldovapops.md;
- Prepared and sent to the Secretariat of the Convention copies of all information and awareness materials, developed within the Project awareness campaign.

In addition, in 2009 one poster, one leaflet and one calendar (for 2010) was developed and printed (to present the project outcomes and to be distributed at national and international level). Was finalized the English version of the film about the project implementation. For the POPs polluted sites clean-up activities, was developed the web site www.cleanup.vox.md.

TO SCHOOLCHILDREN ABOUT PESTICIDES

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Abstract

The XXth century was the age of rapid developments in chemistry and industry. Thanks to them we are using convenient materials and tools. The growth of human population on the Earth and urbanization owe much to the intensive agricultural technologies based on strong chemicalization of farming.

However any invention has two sides of the coin. The Media striving for shocking news or revenue from advertising often delude the public. What is the way out? First of all, a modern person should be knowledgeable and intelligent, able to understand the benefits of the new agent and its threats. After thorough analysis of the situation a group of young ecologists from Green Cross Belarus has developed a workbook. Its aim is to give the children up-to-date knowledge about pesticides and their utilization, their useful and dangerous properties. It also stimulates the children for thoughtful attitude to any “miraculous” invention that awaits them in future.

The workbook is developed for 7 lessons with senior pupils and is oriented on Ecology, Biology, Chemistry and Geography teachers. It includes 7 PowerPoint presentations, a book with applications, tests and questionnaires. The material is divided into 4 sections. <u>Pesticides – allies and enemies:</u> a historical overview of chemical means usage alongside with the definition of POPs and important normative documents and modern standards for pesticide production and storage. <u>Pesticide classification</u>: a flow chart of the most widespread types of pesticide classifications on the basis of their purpose, dates, action mechanisms, etc. <u>Pesticides in the environment:</u> different ways of pesticide penetration into the environment, migration schemes and pesticide influence on the organic world, alternatives to pesticide usage. <u>The influence of pesticides on human health.</u>

Key-words

Pesticides, obsolete pesticides, POP, DDT, education, school, children, teacher, public awareness, population, health, safety, storage, utilization.

Introduction

In the haste of the XXth century the majority of the population didn’t notice the rapid technological revolution in the chemical science and industry. However that is thanks to them that we are using convenient materials and tools for everyday and production purposes. The growth of human population on the Earth and urbanization owe much to the intensive agricultural technologies based on strong chemicalization of farming. In other words the innovations of the past and present centuries are greatly based on the developments in the chemical science.

However any invention has two sides of the coin. Acquiring something we, either consciously or not, pay for it. What is the price for the progress in chemistry? In this article we will focus on a wide range of problems brought to life by the intrusion of chemistry in all the areas of modern production and everyday life, but persistent organic pollutants (POPs) or more concrete pesticides will be in the centre of our attention.

Pesticides (from lat. pestis – infection and caedo – to kill) are chemical substances used to kill weeds (herbicides), pests (insecticides, acaricides, zoocides, etc.), and illnesses of cultivated plants (fungicides, bactericides, etc.). Defoliants, desiccants, phytohormones as well belong to the group of pesticides. The majority of pesticides are synthetic organic substances. When applying persistent highly toxic pesticides systematically, especially in inflated doses, they pollute the environment that leads to the extinction of useful insects, birds, fish and animals as well as to the poisoning of human beings by pesticides themselves or by products in which pesticides accumulate. The usage of pesticides is regulated by law in all the countries.

The book "Silent Spring" by Rachel Carson unexpectedly evoked broad public interest. What was so stirring for the readers? Carson emotionally and convincingly told about the fatal consequences of DDT for the health of living beings. She talked about the birds extinguishing in a whole region as their reproductive capacity was destroyed by high content of DDT. They accumulated in tissues of living beings, the higher in the pyramid of numbers the more the amount of it in the body. This scared people a lot and soon DDT was banned.

It should be mentioned that since 1940s DDT was widely and successfully used for protection from malaria in tropical and subtropical regions. Before its usage malaria used to claim 2-3 million people's lives a year and the number of those suffering from this serious illness was a hundred times higher. Due to decennial usage of DDT in a number of countries malaria subsided. In India the number of diseased descended from 75 million people in 1952 to 100 thousand in 1964, in USSR from 35 million in 1956 to 13 thousand in 1966. World Health Organization (WHO) and the UN attribute 50 million lives saved from malaria to this substance. For the discovery of the miraculous qualities of DDT Dr. Paul Muller was awarded Nobel Prize in medicine in 1948. However in the in the mid-60's DDT was forbidden. What was the result? In Sri Lanka due to the usage of DDT the number of diseased decreased from 2,8 million people in 1948 to 17 in 1964. In five years from the ban of DDT this number quickly reached 2,5 million (1969). It's important to note that in such not tropical countries like Azerbaijan in the late 90's an outbreak of malaria was detected (up to 1000 cases) that was extinguished thanks to the efficient cooperation with WHO.

It is no secret that random usage of pesticides leads to the pollution of huge territories not only in the areas of application but in far beyond their boundaries as well. E.g. it was found out recently that the main ecological threat for the Lake Baikal nowadays is not the pulp and paper plant situated on its bank but the usage of DDT in distant Mongolia that is carried to the lake through thousands of kilometres.

Nowadays the usage of POPs is strictly regulated on international level. From the beginning of the 90's the Protocol of the UN Economic Commission for Europe on POPs and widely-known Stockholm, Basel and Rotterdam Conventions were adopted.

Methodical kit

That is clear that all the results of influence of new chemical substances on people are hardly predicted especially in the long term. Numerous researches disclose only separate mechanisms of impact and often display opposite results.

Though the tropics are far away pesticides in our countries like Belarus as well as other POPs are still widely used partially in agriculture, landscape gardening, flower growing, etc. Something is done under control, something without it. E.g. in rural areas the methods of "chemical weeding" are widely used by individuals to achieve "good" harvest for sale.

What is the way out? First of all we were guided by the concept that every person should be educated and knowledgeable nowadays. He should at least understand the benefits of the new miraculous substance and its threats. Modern mass media striving for shocking news or revenue from advertising often delude the public. In the majority of cases the answer to the question concerning benefits or harm is either definitely negative or definitely positive. In the result a usual person simply doesn’t understand the realms of using chemical substances.

Having analyzed the situation a group of students-ecologists actively engaged in the programs of Green Cross Belarus developed a workbook “To children about pesticides”. Its aim is to give the children up-to-date knowledge about pesticides and their utilization, their useful and dangerous properties. It also stimulates the children for thoughtful attitude to any “miraculous” invention that awaits them in future.
The workbook is developed for 7 lessons with senior pupils and is oriented on Ecology, Biology, Chemistry and Geography teachers. It includes 7 PowerPoint presentations, a book with applications, tests and questionnaires. For better understanding the material is divided into 4 sections.

1. In chapter «Pesticides – allies and enemies»
   a. Several definitions to the term “pesticide” are provided;
   b. A historical overview of chemical means usage is given;
   c. The distinctions between pesticides of first, second, third and fourth generations are examined;
   d. A definition to POPs is given;
   e. Most important international standard acts on pesticides and POPs are enumerated;
   f. Modern requirements for production and storage of pesticides are provided.

2. «Pesticide classification». Nowadays pesticides are used in the majority of spheres of human economic activity ranging from agriculture to aerospace industry. A great number of pesticides are known nowadays. This is because people need pesticides with specific qualities. As the number of pests is large and their species and classes are rather diverse the number of pesticides should be commensurable. And to achieve the necessary result in each specific case pesticides should be classified. Pesticides are qualified on different criteria depending on the necessary quality of the pesticide. In this chapter there is a flow chart of the most widespread types of pesticide classifications on the basis of their:

   a. way of penetration into the body;
   b. action mechanisms;
   c. purpose;
   d. chemical composition;
   e. toxicity;
   f. rate of decomposition in soil.

3. «Pesticides in the environment». Among all the chemical products produced by people pesticides occupy a special place due to their importance in the life of the society as well as to the dangers of being present in the environment. They are consciously brought into the environment by people. It is a necessity as otherwise up to half of the harvest would be lost because of weeds, pests and illnesses, and millions of people in the XX^{th} century would die from malaria and typhus. It is the pesticides that save thousands of human lives from famine and illnesses. It would be impossible to feed 6,5 billion of people without pesticides and fertilizers as only 11% of land on our planet are suitable for farming. Besides pesticides allow to get cheap agricultural products affordable to all. In this chapter

a. different ways of pesticides getting into the environment are shown;
b. the behaviour of pesticides in air, water and soil is examined;
c. the schemes of pesticide migration are provided;
d. the influence of pesticides on animals and plants is analyzed;
e. alternatives to the usage of pesticides are provided;
f. modern requirements to the pesticides are provided;
g. particularities of pesticide usage in Belarus are examined;
h. information about pesticide market in Belarus is provided;
i. the situation with inapplicable pesticides is shown and the ways of its resolution are provided;
j. the data about the situation with inapplicable pesticides in Belarus is provided with types and places of storage indicated.

4. «The influence of pesticides on human health» After the detection of useful qualities of pesticides it was soon also discovered that beside these undoubtedly important qualities they also poses a number of qualities rather dangerous for people and the environment. It was stated that besides insects, coarse fish and undesirable vegetation pesticides strike equally all living beings in the environment – useful insects, planktonic organisms, birds and mammals including human beings. A significant number of alarming facts started accumulating with the onset of DDT usage. When in human body in large numbers pesticides strike almost all organs, causing dystrophic changes in the tissues of varying severity, disturbing metabolism, depressing the function of central and peripheral nervous systems. All the population of the Earth is exposed to chronic influence of minor pesticide doses and its amount depends on the diet, geographical position and the level of industrial development in the area. It was considered before that "dose determines the poison". It meant that small quantities of poison don't lead to any consequences and big doses are lethal. However modern researches state that continuous contacts with small doses are even more dangerous than a single large dose. This concerns pesticides as well. Every day each of us is exposed to micro doses of pesticides that together with other unfavourable anthropogenic factors influence our bodies. In this chapter attention is given to

a. Bioaccumulation of pesticides in human body
b. The influence of pesticides on human beings (direct and indirect), its symptomatology:
    i. acute poisoning by pesticides
    ii. chronic poisoning by pesticides
c. The study of pesticide substances
d. Probable major factors of pathologic changes under the influence of minor pesticide doses.
    i. Pesticide carriage
    ii. Toxicity for organs
    iii. Mutagenicity
    iv. Cancerogenity
    v. Immunotropicity
    vi. Reproductive toxicity
    vii. Embryo-, fetotoxicity, teratogenicity
e. Preventive measures and reduction of pesticide negative influence on health
    i. Measures on governmental level
    ii. Measures taken by any of us

At the end of the workbook there is a glossary, poll list for comparison of children knowledge before and after the course, and various applications for more detailed presentation of information: the data on inapplicable pesticide storages, the table of action of major pesticide classes, acute poisoning symptoms and first aid in acute poisoning.

Application

The workbook has modular structure. The major modules contain basic information topical for any region. At the same time in this workbook there is concrete data on peculiarities of pesticide use in Belarus. This way teachers from other countries and regions can successfully implement this material in their educational activity, supplementing it with concrete data on their region. The complete set of materials of the workbook is available on CD ROM. The language is Russian. Translation into English is planned in the future.

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Special workshop for Central Asia Countries: Problems and Initiatives for Solutions on Obsolete Pesticides

PESTICIDES REGULATION IN GEORGIA

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General condition

During the last ten years, by the result of conducting active environmental policy, the legislation base of directing chemical agents had been developing. A large variety of laws and regulating sub-normative acts are adopted, where particular attention is given to prevent polluting the environment with harmful substances and to safety of health

1. Viena Convention for the protection of ozone layer
2. The Montreal Protocol on substances that deplete the ozone layer
3. Basel Convention on the Control of trans boundary Movements of hazardous wastes and their disposal
4. The Paris convention on the prohibition of Chemical weapons of 1993 placed a total and definitive ban on these weapons
5. Rotterdam Convention
6. Stockholm convention on Persistent Organic Pollutants
7. International code of Conduct on the Distribution and use of pesticide (FAO 2002)

For Georgia, as for an agrarian country, problem of plant protection ecology is very urgent. The phyto sanitary situation becoming worse and by influencing of harmful organism the lost of harvest had reached to30-50 %. Following from the created heavy economic condition, inculcation of integrated security system in farms, safe and effective usage of chemical agents accounts for as guarantee of food safety of country .

There is rather developed legislation of pesticides, where questions about registration, licensing, import, conservation, realization, usage and information spreading, limitations, sanitary and ecological safety general rules.

Usage of pesticides and their circulation are regulated in agriculture by legislation of Georgia about "plant protection from harmful organisms" and "pesticides and Agrochemicals", also according normative acts. It is permitted to import, movement and usage only these pesticides, which had underwent biological , hygiene-toxically and ecological examination and demonstrative field exams, are registered and added to "pesticides permitted to use in Georgia , State catalogue ", that is kept by Ministry of Agriculture. The Ministry of Environment Protection and Natural Resources, Ministry of Health, Labor, Social Protection of Georgia are actively involved in the process of evaluating and choosing of pesticides. At the present time about 150 substances in force and about 300 extensively operating preparative form. These chemicals are added to the list registered Euro Union- in first enclosure of 91/414/ECC directive or in USEPA registered list of active substance.

These pesticides, which are regulated by Rotterdam Convention and by Stockholm Convention, are added to the list of "prohibited and strictly limited substances" in Georgian territory. Till 2005 importing and trading of pesticides had been regulated by permission and license, which would be issued by the Ministry of Agriculture. At the present time issuing of permission on importing, producing and turnover by the Ministry of Environment Protection and Natural Resources are defined only for limited turned over materials (where prohibited and strictly limited pesticides were included) by the Georgian Law about "licenses and permissions ".

Using of pesticides in Georgian agriculture sensibly reduced comparatively with Soviet period. According to the data of Statistic Department of Georgia, in 2006 the area of 1 year plantations treated with pesticides, were consisted totally 52,3 thousand h. , and treated perennial plantations area were consisted with -84.7 thousand h., in our country there are totally about 700000 h. arable land and 150000 h. perennial plantations. About 40 % have been treated.

Pesticides are not produced in Georgia. Pesticides are imported in the country from leading firms of Europe, USA, India and Turkey (Singenta , Bayer, Basf, Dupon, New farm, Izagro, Dau agroscience, FMS-Europe, Detia Degish, Parijat, Safa tarim, Hectashi an etc.)

Comparing with Soviet period , when 37000 tones of pesticides had been importing in Georgia in an year for planned treatment of agricultural plants and Georgia was on it's 8 position with usage of pesticides among the Soviet republics, during the last tenth years 1000-3000 tones of pesticides have been importing in the country in an year. It is caused as from the consumers low demand in the country following from the existing heavy economic conditions, so that new generation environmentally relatively safe pesticides could be used plenty low spending standards. In result stocking of pesticides are sharply reduced on economic area. Is not used chlorine organic, mercuric pesticides, Herbicides of Triazine group, using of phosphorus organic insecticides is sharply reduced.

Importing of pesticides (in tones) in Georgia by years:

1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
1660	1890	940	450	1726,5	2083	1794,5	3756	1008,2	802,025	1050

Fungicides are about 50% from imported quantities of chemical pesticides. Using of Fungicides keeps 58 % in the country, insectoacaricides 35% , herbicides 5%, seeds treatment preparations 2%. Import of biological agents is stopped. Plant protection service uses biological agents in measures to liquidate hazardous depredators (fall webworm)

Exporting and re exporting plant protection agents from Georgia implements in unimportant quantities.

As for pesticides residues, market this sphere. Importers and traders , which are private persons , purchase by their means such number of chemicals, for which they have real buyers and practically there are no residues .

Priority problems regarding to chemicals in Georgia

Food pollution- hexachlorocyclohexane, metabolites, nitrate, nitrosamines, benzene, aflatoxins, desoxynivalenol, hydroxymethyl furfurol, penicidins designate in foods;

Water pollution – pesticides total amount designate in the water.

Pesticides Uncontrollable and illegal import and realization were a big problem in 90-es after fail of the Soviet Union when supply of pesticides centralized way were disordered and unregistered and obsolete pesticides had been imported in the country. State registration and control system was established in the country after 1998 when the law of Georgia about "pesticides and agrochemicals "enacted. Ministry of Agriculture and Ministry of Environment Protection and Natural Resources are actually involved in this system.

As for pesticides import, at the present time Ministry of Agriculture carries out quarterly monitoring and is acting with customs service, they execute according with “State catalogue of pesticides and agrochemicals“ when goods crosses the border. Also carries out annual monitoring of officially existed trading lines (151 pesticides and agrochemicals stores).

Besides, pesticides and agrochemicals importers/exporter, distributors, keepers and manufacturers registry is created by the National Service of Food Safety, Veterinary and Plant Protection of the Ministry of Agriculture which is responsible on control of use and trade with pesticides.

Ministry of Agriculture in 2005-2008 had issued 12 normative acts to regulate pesticides and agrochemicals effective use and safe consumption sphere, among them: “about rules on use, storage, transportation and realization of pesticides and agrochemicals“, “rules of pesticides and agrochemicals labeling “, “rules on small packing of pesticides” and etc.

Accumulation of unfitted pesticides – this problem has been formed in Soviet period, when planned treatment of agricultural areas took place. At the same time by the result of active working of health protection state bodies, permitted pesticides lists had been overviewed annually and hazardous preparations for humans and environment had been prohibited, withdrawn and put into secure landfills or kept in store houses.

After this period more then 3000 tones of obsolete, unfitted pesticides had been gathered among which are POPs, mainly representatives of Chlororganic group, hexachlorocyclohexanes and others. Especially complicated condition is related to Ialghuji landfill, because inactivation and rehabilitation requires much funds and decision of this condition is possible only within international projects or State planned programs.

Part of pesticides were placed as in central so in former collective farm little store houses, most of which are destroyed. Pesticides in most cases are under open-sky, packing is damaged, analyzing and identification is often impossible, cleaning of mentioned territory requires planning a number of measures and implementation.

As we mentioned, at the present time the problem of accumulation of pesticides does not exist in Georgia, because this topic is regulated by presented market and consumers low demand, because of this importing of pesticides in over normative quantities in the country by private enterpriser does not happen. This kind of problems could be exist, when by the results of strict control of any useless chemicals would be discovered, or hazardous preparations would be withdrawn from the registration or importing, realization and use of them would be limited in the point of environment and humans health protection. In this case it is very important to be existed storehouses (having of two storehouses- one in West another in East of Georgia is recommended) where the withdrawn pesticides would be safely disposed, until the way of their destruction would not be found.

Facts of health damage among the agricultural workers really exist; chemical intoxication / suicides single accidents had been discovered in various regions of Georgia. As a pesticides registration agency, National Service of Food safety, Veterinary and Plant Protection has information about all registered and permitted pesticides suited for use, among them: NSDS, where is defined the safety measures of pesticides storage, transporting, usage and during the fire and emergency occurrence. This information, also a determining method of pesticides operating substance is accessible for everyone.

Researching and nongovernmental organizations are acting in agricultural field for chemicals management. They traditionally conduct research of pesticides and agrochemicals, and recently created NGOs which have pesticides small data base are involved in this process. At the present time a private laboratory is accredited by the accreditation centre of Georgia, which has all means (material-technical and trained personnel, methods of proper determination) to determine agrochemicals sort and quantity in products, vegetables, soil and water. There are also laboratories in research Institutes, equipped with older technique but with trained and experienced personnel.

Examinations of chemicals are performed during the process of their State recording on the basis of law about "pesticides and agrochemicals" and "regulation of pesticides and agrochemicals testing, examination and recording". 5 kinds of examinations are conducted by the high ranged experts of research institutes: biological, hygiene-toxiferous, ecological, ichthyo toxiferous, veterinary-sanitary (documental, laboratorial and field examination). Pesticides could be recorded only in case of experts' positive conclusion and by the coordinated decision of three Ministries: Ministry of Agriculture, Ministry of Environmental Protection and Natural Resources and Ministry of Ministry of Labor, Health, and Social Affairs. Chemicals research at the present time is conducted by Agronomical profiled institutes and joint-stock company- Medically Profiled Institute, existing in the system of Ministry of Education and Science. This Institutes and some nongovernmental organizations have possibility (have highly qualified personnel) to conduct trainings relating to chemicals.

Accumulation, packing and placement in safe temporary places of obsolete and unfitted pesticides

One of the problems of environment protection are delayed and useless pesticides and persistent organic pollutions (POPSs), as in Georgia so in many other countries. Georgia joined the "Stockholm convention on Persistent Organic Pollutants" at April 11, 2006.

In the frames of the convention in Georgia was implemented a program "on Persistent Organic Pollutants to prepare national operating plan in aim to implement Stockholm convention". The projects main aim was to create and develop persistent abilities to implement Stockholm convention's requirements. The project included inventory the POPS, society information about plural problems of POPS, and preparing POPS operating plan in Georgia.

Under the project in hole country had been taken stock on 3057 tones of pesticides, and 2700 tones among it supposedly is placed in Iaghluji pesticides landfill, and the rest 357 tones are distributed to chemicals storehouses on whole territory of country.

By tacking stock of polychlorinated biphenyls 216 transformers were displayed, where in 623 tones of polychlorinated zeds are placed, which contains biphenyls, and whole weight of implements is about 2000 tones. 200 tones of oil containing PD are also supposedly placed in condenser.

By stock-tacking was discovered that about 80% of dioxin-furan spray is uncontrolled burn process (burning remains on the trash places and forest fires), other 20% is production process.

The project of national plan about persistent organic pollutants is ready, which is widely considered along with interested parties and is introduced in The Government of Georgia for affirmation.

In 2007-2008 two programs were implemented in the frames of the convention:

"Gathering, packing and sending to safe temporary place of delayed and useless pesticides", funded by state budget.

Within the project highly ventured facilities which were polluted with toxic chemical were cleaned. 50 tones of delayed and useless pesticides were gathered, packed and sent to specially prepared place. 130 tones of polluted ground also were removed from facilities, which were placed in Ialghuji toxic chemical testing ground, according to the environmental rules. Mentioned program had been proceed at the present year and supposedly 60 tones of delayed and useless pesticides and polluted ground would be placed safely.

"Reducing venture of delayed pesticides in Kakheti region". The project was sponsored by Dutch government and was implemented by Dutch international organization "Milieukontakt International". Within the project a store house was repaired for placing delayed and useless pesticides. Were cleaned 7 highly ventured facilities, were removed 117 tones of delayed pesticides and 105 tones of polluted ground and were placed safely.

By the financial support of the Global Environmental Fund and on UNODC environmental programs and health care world organization initiative, are being conducting preparatory works in Georgia according to the project, "DDT demonstration of alternatives, evaluating and introduction against the carriers of malaria and other diseases". Mentioned project is regional and covers some countries of Central Asia and North Caucasus. The project is encouraged by the Ministry of Environment Protection and Natural Resources and the Ministry of Ministry of Labor, Health, and Social Affairs.

The Ministry papered draft project "Safe placement of Persistent Organic Pollutants in Georgia", which is submitted to the Global Environmental Fund. Mentioned designing offer basically contains proper collaboration of regulator documents and subject of reduction of delayed Persisting Organic Polluting pesticides, which means gathering of existing POPS pesticides, placing in secure place and finally destroy of these pesticides.

Posters

ANAEROBIC BIOREMEDIATION OF SOIL CONTAMINATED WITH CHLORINATED PESTICIDES: LABORATORY EXPERIENCE

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Abstract

Results of lab-scale tests on anaerobic bioremediation of polluted soil from pesticides "tombs" area, using methanogenic granular sludge as inoculum are presented. Experiments with soils contaminated with organochlorine pesticides: γ-HCH, DDT and methoxychlor, collected at three "tombs" in central Poland, demonstrated that it is possible to effectively remove these compounds. In case of DDT removal accumulation of DDD was significantly smaller than resulting from stoichiometry, suggesting further degradation of this metabolite. To provide more insight into bioremediation process, next experiments using selected soil sample were performed. Prolonged incubation showed that removal proceeded rapidly during first 2-4 weeks. Afterwards, residual concentrations of pesticides remained unchanged until the end of 16-week experiment. Solid-phase extraction using Tenax TA suggested that persistency of these residues was caused by their resistance to desorption, perhaps resulted from pollution aging process. DDD transformation was confirmed by appearance of dichlorobenzophenone (DBP), final product of DDT anaerobic biodegradation. Additional studies indicated that residual concentrations of pesticides and intensity of DDD conversion, which in turn affected accumulation of this metabolite, strongly depend of process temperature. Use of nonionic surfactant Tween 80 could also decrease residual levels of some compounds and stimulate DDD transformation. Dose of surfactant should be optimized however, as higher concentration was found to negatively affect this DDD conversion.

Keywords: DDT, γ-HCH, methoxychlor, soil bioremediation.

Introduction

Clean-up of obsolete pesticide dumping sites (such as "tombs") is mostly aimed at removal and disposal of chemical waste. Less attention is paid to surrounding areas of polluted land and groundwater. Although the most contaminated soil is mostly excavated and transported to hazardous waste landfills, such procedure is not completely satisfying from the environment conservation point of view. Moreover, less polluted areas are usually (due to cost problem) left undisturbed, still posing an ecotoxicological risk.

In Polish conditions, typical main contaminants of "tombs" areas are chlorinated pesticides: HCH isomers, DDT and methoxychlor. Persistence of these pollutants makes soil remediation difficult. However, it was demonstrated that they can be anaerobically dechlorinated to simpler compounds, more prone to subsequent aerobic biodegradation [1-3]. The presented research was focused on use of methanogenic granular sludge (biomass from anaerobic reactors treating wastewater, already shown as effective biocatalyst of dechlorination – e.g. [4]) as inoculum in the first, anaerobic phase of bioremediation of such soil.

Materials and methods

Soil samples were collected at three pesticide "tombs" in central Poland: Bogomilow and Sepno-Radonia (Lodz voivodship): BOG4, BOG5, SEP2 and SEP5; Mlynow (Wielkopolskie voivodship): MLY2. Sampling points were located at or below concrete tanks forming the "tombs" structure. BOG and MLY samples were classified as sand, with little organic matter

(SOM); SEP soils were sandy clay loam/clay loam with 2-2.7% SOM. Samples were air dried and sieved, then refrigerated until used. Granular sludge came from anaerobic reactor treating wastewater from a soft drink factory. Prior to use, it was thoroughly rinsed with tap water on a 0.25 mm sieve to remove fine particles and decay products.
Bioremediation tests were prepared in 120 ml serum bottles, using 3 g of soil and 1 g of sludge (wet mass), diluted with 30 ml of mineral medium (after [5], without yeast extract). 20 mM lactate was added as electron donor. The bottles were tightly capped and headspace was exchanged to 80% N_2/20% CO_2 with overpressure. The bottles were then incubated in the dark statically (shaken by hand once a week only). All tests were done in triplicate.
For extraction, soil and sludge slurry was filtered through paper filter, and the solids were left to dry. The filtrate was extracted by 15-minute shaking with 16-ml volume of hexane, previously used for rinsing the sample bottle. Solids and the filter were extracted with 16 ml of hexane/acetone in tightly closed 40-ml amber vial by heating to 70ºC for 4 h. The extract was then centrifuged with small amount of anhydrous sodium sulfate. For all extracts, decachlorobiphenyl was used as surrogate standard. Pesticides measurements were performed after dilution of extracts, using GC-ECD.
Samples for Tenax solid phase extraction (SPE) were prepared as above, using only 1 g of soil and 0.33 g of sludge. The SPE procedure was based on [6]. Soil slurry was transferred into a separatory funnel, spiked with 0.15 ml of 10% sodium azide (microbial inhibitor) and then shaken with 0.5 g of Tenax TA beads. At set times the slurry was drained into a new separatory funnel and shaken again with fresh Tenax. After 72 h SPE, the slurry was analyzed for residual pesticides. The desorbed pesticides were measured by extracting the Tenax grains remaining in the used funnel by shaking them with 16 ml hexane.

Results and discussion
First series of experiments involved bioremediation tests with different soils, incubated for 3 weeks at 30°C. Results are given in Tab. 1.

Table 1. Results of 3-week anaerobic bioremediation at 30°C (average and standard deviation given in parenthesis, all data as μmol/kg dry soil; upper before, lower after incubation).

sample	γ-HCH	p,p’-DDE	p,p’-DDD	p,p’-DDT	methoxychlor
BOG4	0.99 (0.12)	0.13 (0.02)	0.09 (0.02)	0.98 (0.14)	0.96 (0.18)
	0.04 (0.00)	0.06 (0.01)	0.21 (0.03)	0.20 (0.05)	0.17 (0.03)
BOG5	1.35 (0.07)	0.18 (0.03)	0.42 (0.11)	3.82 (0.45)	1.71 (0.14)
	0.11 (0.06)	0.51 (0.40)	1.06 (0.19)	1.73 (0.15)	0.61 (0.04)
SEP2	19.6 (0.68)	0.69 (0.07)	3.53 (0.79)	97.2 (7.15)	17.4 (0.81)
	0.34 (0.01)	0.43 (0.17)	19.2 (1.71)	12.1 (1.15)	0.58 (0.18)
SEP5	2.20 (0.05)	BDL	BDL	8.21 (0.95)	3.31 (0.33)
	0.17 (0.12)	BDL	2.15 (0.15)	1.03 (0.38)	0.18 (0.13)
MLY2	0.32 (0.00)	0.13 (0.03)	4.52 (0.31)	11.11 (2.20)	1.59 (0.17)
	0.06 (0.00)	0.03 (0.00)	3.13 (0.36)	0.49 (0.05)	0.49 (0.03)

BDL – below detection limit

There was a significant loss of pesticides γ-HCH and methoxychlor occurring in all soil samples. p,p’-DDT was also greatly removed, and its removal was accompanied by formation of p,p’-DDD, with p,p’-DDE level little changed. It should be stressed that amount of newly

formed p,p'-DDD was in all cases considerably lower than that corresponding removed p,p'-DDT, which suggests further degradation of this metabolite. This is important as DDD is also toxic and persistent, and standards of soil quality usually refer to collective sum of DDT and its primary degradation products DDD and DDE.
To elucidate the course of the process next tests was done on SEP2 sample, with long 16-week incubation at 22°C with periodical sampling. This lower temperature was chosen as approximately corresponding upper range of soil temperature in Polish conditions. Results of this test are presented in Fig. 1.

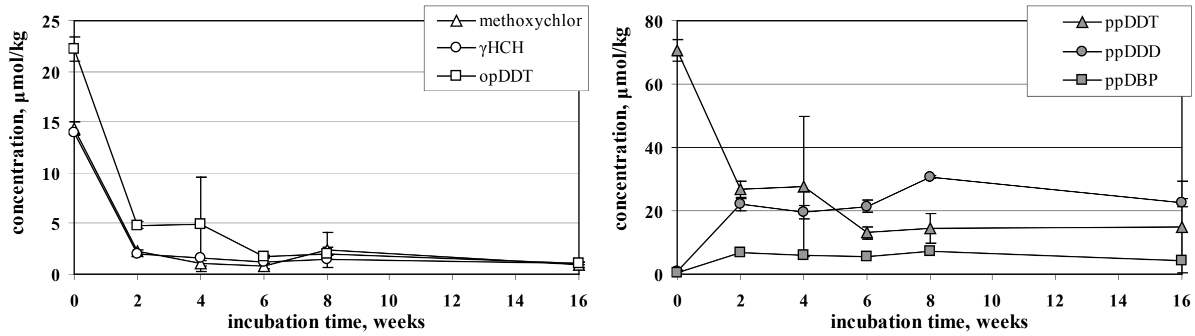

Figure 1. Concentration of pesticide (metabolite) during 16-week bioremediation of SEP2 soil (error bars represent standard deviation, may be covered by symbols).

It was shown that removal of γ-HCH, methoxychlor and o,p'- and p,p'-DDT proceeded quite rapidly during the very first period of incubation, and it was practically completed within 4, maximally 6 weeks. Afterwards residual pesticide concentrations remained practically unchanged until the end of experiment. Degradation of p,p'-DDD metabolite was confirmed by appearance of p,p'-dichlorobenzophenone (DBP), the terminal product of anaerobic degradation of DDT [2]. However, this transformation seemed also to occur mainly in the first two weeks. After that time, concentrations of both metabolites did not vary much.
Additional bioremediation tests (data not shown) with repeated addition of sludge, electron donor or alternative electron acceptor (sulfate) excluded metabolic limitations as possible causes of pesticides (metabolites) residuals persistence. Therefore, it was hypothesized that this phenomenon was linked to availability limitations. To verify that, in the next experiment bioremediated SEP2 soil was sequentially extracted using Tenax TA sorbent, after 0, 2, 4 and 6 weeks of incubation at 22°C. Tenax SPE is often applied to determine desorbability and extent of sequestration of hydrophobic organic contaminants (HOCs) in soil [6]. The results of this test are given in Fig. 2.
The results confirmed this supposition. At the start of the test the originally present pollutants (γ-HCH, methoxychlor, p,p'-DDT) were in major part easy desorbable, with only minimal fractions resistant to desorption. After bioremediation, the unremoved pesticides were mostly hardly desorbing fractions, and this tendency was even more distinct with the progress of incubation. This finding is consistent with reports on bioremediation of other HOCs, like PAHs, where stalling of their removal was ascribed to slow desorption of their fractions bound to the soil matrix (e.g. [7]).

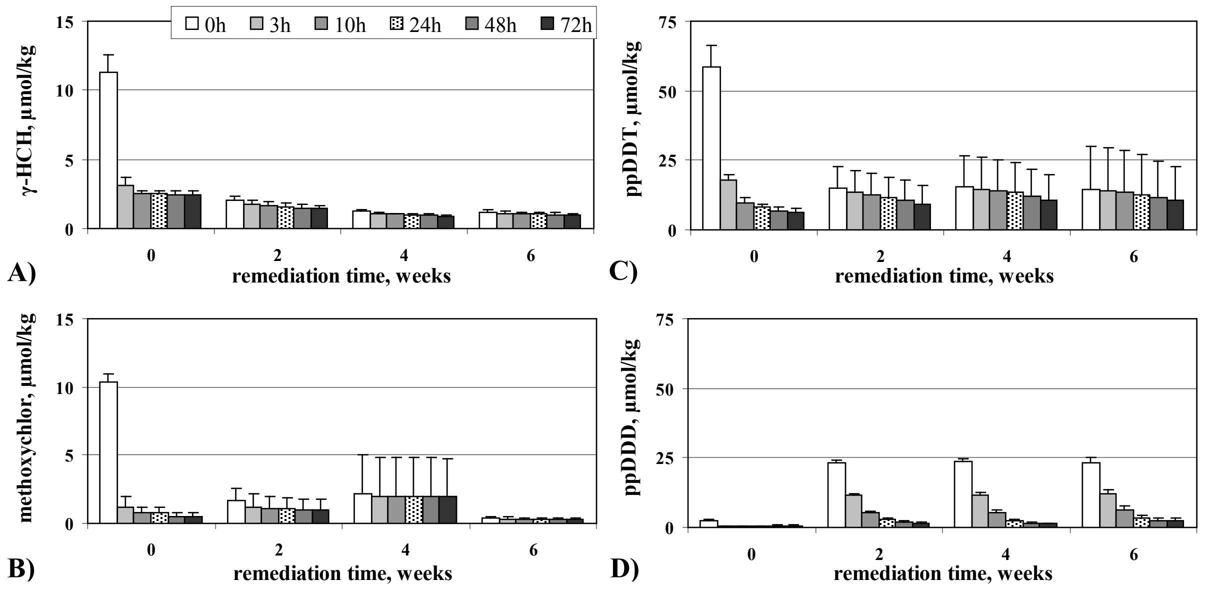

Figure 2. Pesticide remaining in soil after 0, 3, 10, 24, 48 and 72 h of Tenax solid phase extraction: A) γ-HCH, B) methoxychlor, C) p,p'-DDT, D) p,p'-DDD.

However, newly formed p,p'-DDD product was quite easily desorbable throughout the whole experiment, and despite that it was effectively degraded only in the first period of incubation (see Fig. 1). As additional test, mentioned above, excluded some metabolic constraints as possible reasons, the mechanism of its persistence is still unclear.
In a search for enhancing the performance of the process, next experiments aimed at the effect of surfactant addition (Tween 80) and influence of temperature. These tests involved 8-week incubation with sampling every two weeks. Only the final data are given for brevity (Fig. 3).

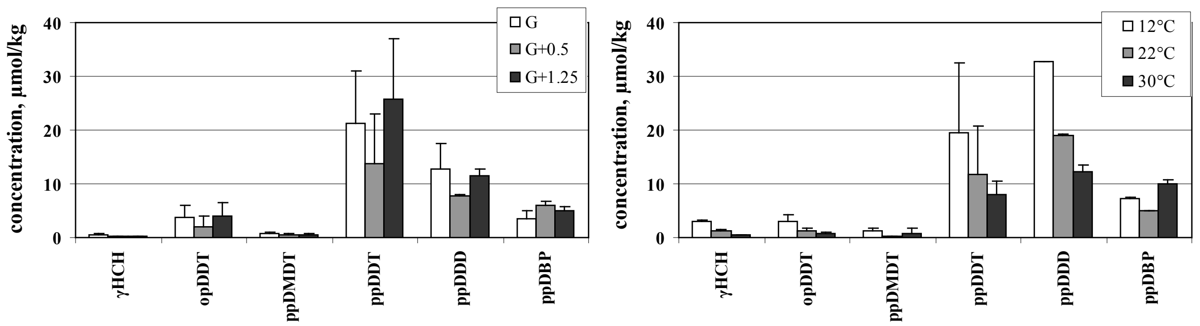

Figure 3. Concentration of pesticide after 8-week bioremediation (ppDMDT - methoxychlor). Left – test at 22°C with Tween 80 (G – samples with sludge only, G+0.5 – sludge + 0,5 mM surfactant, G+1.25 – sludge + 1.25 mM surfactant). Right – test at different temperatures.

Addition of 0.5 mM Tween 80 (concentration in the liquid phase) resulted in decrease of residual concentrations of originally present pesticides as well as in intensification of DDD transformation, producing lesser accumulation of this metabolite and higher formation of DBP. Reduction of residual concentrations was probably the effect of partial release of bound fraction due to surfactant interaction with soil matrix [8]. As for lower DDD accumulation, such findings were already reported [9, 10]. However, higher concentration of surfactant (1.25 mM) resulted in adverse effect, which stresses the necessity of surfactant dose optimization.
Temperature rise also considerably diminished residual concentrations and DDD accumulation. The former effect was supposedly caused by increase in desorption rates.

Cornelissen et al. [11] have demonstrated that temperature strongly influenced desorption of slowly and very slowly desorbing (bound) fractions of HOCs.

Conclusions

Inoculation with granular sludge proved to be effective method of anaerobic primary bioremediation of chlorinated pesticide contaminated soil, allowing for high removal of γ-HCH, DDT and methoxychlor. Their removal efficiency is limited by persistence of residuals, being desorption resistant fractions of these pollutants, probably resulting from "aging" process. DDT metabolite DDD is partly removed; however its accumulation is still high enough to make removal of DDT/DDD/DDE moderate. The effectiveness of the process could be improved considerably by increasing temperature, although such treatment could be problematic in field conditions. The more suitable method of performance enhancement seems to be addition of optimized surfactant dose.

As anaerobic transformation of chlorinated pesticides is not complete and results in intermendiates (for example DBP), the aerobic post-treatment is necessary.

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PRINCIPAL COMPONENT ANALYSIS ON THE BASIS OF PERSISTENT ORGANIC POLLUTANTS AND MORPHOLOGICAL PARAMETERS OF BALTIC HERRING (CLUPEA HARENGUS MEMBRAS L.) FROM THE GULFS OF FINLAND AND RIGA

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Baltic herring (Clupea harengus membras L.) is the most important fish species in the Baltic and for the Estonian fish processing industry. Consequently, the presence of toxicants in this species and in fish in general is of concern from the point of view of human health. The morphological parameters (length, gender, weight, maturity of the gonads) and fat content in herring muscle tissue, used on the shorting, should be considered as a basic for statistical classification according to the catching time and place. The time and place of catch, i.e. the population location, play an important role when different regions are compared.

Keywords: principal component analysis (PCA); persistent organic pollutants (POPs); Baltic herring; Baltic sea; Estonia.

1. Introduction

Persistent organic pollutants (POPs) are a group of toxic and persistent chemicals whose effect on human health and on the environment include dermal toxicity, immunotoxicity, reproductive effects and teratogenicity, endocrine disrupting effects and carcinogenicity. Since Baltic Sea fish generally contain higher levels of persistent organic pollutants, then any other food category, diets containing higher amounts of fish may be expected to lead to higher POPs intakes. In Estonia the content of persistent organic pollutants (POPs) [1–3] and heavy metals [4] in ecological system of the Baltic Sea have been studied since 1974. Since 1994, the analyses of hazardous substances originated from Baltic fish are part of the Estonian National Environmental Monitoring Programme [5–6] When designing research programs for studying environmental pollutants, it is important to consider the need of both chemical and biological precision.

2. Materials and methods

The fish for determining the level of POPs were collected during the period from September, October 2003 to September-October 2005 from three regions of Estonia's coastal sea – the western and eastern parts of the Gulf of Finland and from the Gulf of Riga. The fish for testing was caught using industrial trawlers. The amount of material, necessary for chemical testing, was relatively large – 200 g. therefore, each samples contains from three/four to a score specimens, the exact number depends on the size of the fish. The fish samples were frozen promptly following examination and selection. The length, gender, weight, maturity of the gonads of the fish was determined. Otoliths were removed to determine the age of the fish. The head, tail fin and viscera were removed from the analyzed fish.

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The general method for analyses of the fish samples is described by [7–9]. 10g of herring muscle samples were homogenised with Ultra-Turrax homogenizer in the mixture of acetone – n-hexane solution (30 ml) and extracted in ultrasound bath. The samples were filtered on glass filters, washed with n-hexane and acetone was washed out by adding two times 20 ml of distilled water. After removing the acetone-water phase n-hexane extracts were dried with Na_2SO_4 , the solvent evaporated and lipids weight determined. 2,3,3',4,4',5,5'-heptachlorobiphenyl was added to fat as the internal standard. Lipids were hydrogenolysed with concentrated H_2SO_4 and the last remaining lipid portion removed on a small silica/H_2SO_4 column in a Pasteur pipette. n-Hexane was replaced with isooctane, 7 PCB isomers (CB28, CB 52, CB101, CB118, CB153, CB 138, CB180) and α-HCH, HCB, γ-HCH, 4,4'-DDE, 4,4'-DDD and 4,4'-DDT were analysed using capillary gas chromatography (Varian 3380 with a 100 m DB-5 column) with ECD. LOQ of the method was 1μg/kg fresh weight and expanded uncertainty near the detection limit – 24 – 56%. All fish samples were analysed in a laboratory of the Estonian Environmental Research Centre, accredited by the German Accreditation Bureau (DAP-PL-31.31.00 - 2008-11-22) for organochlorines analyses in environmental samples.

3. Results and discussion

Authors selected the Baltic herring (Clupea harengus membras L.), because they can be caught in all parts of the Baltic Sea and are an important commercial species. The results obtained provide a basis for the hypothesis about the uniqueness of herring populations, there are 14 herring populations around the Baltic Sea [10]. Four spring spawning herring populations are distinguishable in Estonian waters: populations of the Gulf of Finland, Gulf of Riga, northern sea herring (in the island Hiiumaa area) and eastern sea herring (in the Irben Strait – island Saaremaa area). The two last units are rather closely interrelated [8,10,11]

The authors quickly acknowledged the fact that the content of organochlorine compounds in herring of different regions, years and fat content may vary on very large scale. Therefore, aside from the chemical parameters, the biological parameters should also be determined. Aside from fish age, other characteristics – its length, sex, weight, fat content, maturity, etc., are to be taken into account in studies of the POPs in the Baltic fish organism [1–3,12,13]. Basic differences between populations (in morphological features, maturation cycle [14,15], spawning time and place [8,12,13], year-class [15–19], growth rate) are related with differences in the main environmental factors, i.e. temperature, salinity, ecosystem structure etc. prevailing these areas [8,11,20].

The herring parameters determine the coordinates in the formal high-dimensional space. As the database is too large, there is extremely difficult to detect any simple interpretable interrelations in it. The principal component analysis (PCA), mathematical method created by Karl Pearson, can help us to solve our problems. The main goal of PCA is to reduce a number of substantial parameters describing the nature phenomena under survey and find out at least some rules of simplified dynamics. In that way PCA is a transformation of a set of n correlated variables into linear combinations of a set of n pair-wise uncorrelated variables called principal components (PC = eigenvectors of correlation matrix). PCA rotates the cloud of data points such, that the maximum variability is visible. The hierarchy of components is constructed so that the first PC explains the largest amount of total variance in the data and will be correlated with at least some of the observed variables. The second component will also be correlated with some of the observed variables, mainly with these that did not display strong correlations with the first component. The relative significance of each component is indicated by its eigenvalue. The eigenvalue of correlation matrix associated with each PC vector is the variance in that direction. The first component is the eigenvector of correlation

matrix, which corresponds to the highest eigenvalue. As usual, the first two or three components have an eigenvalue larger than one, which is a commonly used criterion for inclusion. The total variance (and the sum of eigenvalues) in that correlation matrix is equal to the number of variables. The proportion of each PC (Tables 1–2) can be calculated as eigenvalue divided with the number of variables.
KyPlot 2.0 15□ software was used to perform PCA at first for all chemical data set and then separately for its groups. In tables 1 and 2 we can notice the first component prevailing. For all new first component sets we have positive correlations (Principal Component Loadings from Correlation Matrix) with initial (measured) data and so the first component represents them all. The second PC separates from POPs list CB 28, HCB, α-HCH ja γ-HCH and the third component CB 28 and CB 52 [21,22].
Figure 1 and Figure 2 represent intercorrelations between the first standardized principal component scores and lipids content. The clusters by years and regions become detached. Calculating means in groups of years and locations the strong interconnection is clearly visible (Figure 3).

4. Conclusions

An important role is played by the time and place of the catch, i.e. the population location, when different regions are compared. The content of POPs in herring, of different fat content and from different regions may vary on very large scale. Therefore, aside from the chemical parameters, the biological parameters should also be analysed. Aside from fish age, other characteristics, length, sex, weight, fat content, maturity, etc., are to be taken into account in studies of the POPs in the Baltic fish. The results do not eliminate the need to monitor the toxicants in fish also in the future, because the use of hazardous chemicals in the Baltic Sea region will probably continue.

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Table 1. Eigenvalues, proportions and principal component loadings from correlation matrix for components 1–4 for all years and regions.

		Comp. 1	Comp. 2	Comp. 3	Comp. 4
All years and regions	Eigenvalue	8,97	1,29	1,06	0,47
	Proportion	0,69	0,1	0,08	0,04
	Principal Component Loadings from Correlation Matrix				
	CB28	0,39	0,21	0,86	0,17
	HCB	0,71	0,42	-0,32	0,16
	aHCH	0,64	0,7	-0,13	-0,09
	gHCH	0,78	0,51	0,05	-0,19
	CB180	0,77	-0,08	-0,12	0,56
	CB101	0,93	-0,24	0,04	-0,16
	CB118	0,91	-0,27	-0,03	-0,13
	CB138	0,93	-0,26	-0,02	-0,09
	CB153	0,9	-0,31	-0,02	-0,01
	CB52	0,84	-0,04	0,39	-0,06
	pp'DDE	0,95	-0,11	-0,05	-0,01
	pp'DDD	0,95	-0,02	-0,11	-0,01
	pp'DDT	0,91	-0,04	-0,13	0,03

Table 2. Eigenvalues, proportions and principal component loadings from correlation matrix for components 1–4 for years and regions.

		Comp. 1	Comp. 2	Comp. 3	Comp. 4
Year 2003	Eigen Value	7,68	1,85	1,28	0,78
	Proportion	0,59	0,14	0,1	0,06
	Principal Component Loadings from Correlation Matrix				
	CB28	0,45	-0,3	0,77	0,19
	HCB	0,4	0,75	-0,29	-0,12
	aHCH	0,43	0,83	0,23	0,18
	gHCH	0,67	0,51	0,45	0,12
	CB180	0,46	-0,11	-0,41	0,77
	CB101	0,93	-0,19	0	-0,14
	CB118	0,92	-0,14	-0,13	-0,09
	CB138	0,95	-0,15	-0,11	-0,05
	CB153	0,88	-0,25	-0,2	0,05
	CB52	0,82	-0,3	0,29	-0,03
	4,4'DDE	0,94	0	-0,08	-0,04
	4,4'DDD	0,93	0,12	-0,1	-0,18
	4,4'DDT	0,82	-0,02	-0,14	-0,15

	Comp. 1	Comp. 2	Comp. 3	Comp. 4	
Eigen Value	7,59	1,86	1,41	0,92	Gulf of Riga
Proportion	0,58	0,14	0,11	0,07	
Principal Component Loadings from Correlation Matrix					
CB28	0,11	0,54	0,71	0,33	
HCB	0,56	0,39	0,05	-0,58	
aHCH	0,22	0,84	-0,41	-0,07	
gHCH	0,58	0,72	-0,28	0,11	
CB180	0,92	-0,09	0,08	-0,05	
CB101	0,79	-0,07	-0,17	0,32	
CB118	0,97	-0,08	0,01	0,02	
CB138	0,96	-0,19	0,05	-0,16	
CB153	0,95	-0,18	0,08	-0,19	
CB52	0,59	0,17	0,7	0,09	
4,4'DDE	0,93	-0,19	0,06	-0,21	
4,4'DDD	0,91	-0,17	-0,2	0,17	
4,4'DDT	0,77	-0,1	-0,28	0,45	

Year 2004	Eigen Value	6,89	2,35	1,58	0,83	Eigen Value	7,77	2,4	1,01	0,72	Gulf of Finland western part
	Proportion	0,53	0,18	0,12	0,06	Proportion	0,6	0,18	0,08	0,06	
	Principal Component Loadings from Correlation Matrix					Principal Component Loadings from Correlation Matrix					
	CB28	0,62	0,11	0,35	0,66	CB28	0,49	-0,47	-0,02	0,71	
	HCB	0,53	0,64	-0,42	0,22	HCB	0,59	0,76	0,1	-0,01	
	aHCH	0,41	0,75	0,47	-0,13	aHCH	0,77	0,51	0,16	0,14	
	gHCH	0,05	0,78	0,48	-0,34	gHCH	0,8	0,49	-0,11	0,18	
	CB180	0,83	-0,04	0,38	0,17	CB180	0,45	0,2	0,74	0,11	
	CB101	0,94	-0,21	0,06	-0,04	CB101	0,87	-0,45	-0,03	-0,03	
	CB118	0,77	-0,49	0,08	-0,13	CB118	0,84	-0,43	0,02	-0,25	
	CB138	0,87	-0,39	0,25	-0,06	CB138	0,78	-0,57	0,14	-0,07	
	CB153	0,9	-0,34	0,2	-0,11	CB153	0,85	-0,43	0,2	-0,1	
	CB52	0,58	0,4	-0,41	0,21	CB52	0,72	0,02	-0,54	0,1	
	4,4'DDE	0,88	0,09	-0,37	-0,11	4,4'DDE	0,94	-0,04	-0,07	-0,12	
	4,4'DDD	0,75	0,1	-0,51	-0,18	4,4'DDD	0,91	0,22	-0,04	-0,22	
	4,4'DDT	0,79	0,14	-0,11	-0,24	4,4'DDT	0,85	0,35	-0,23	-0,02	
Year 2004	Eigen Value	5,65	2,88	1,25	1,09	Eigen Value	11,1	0,85	0,41	0,29	Gulf of Finland eastern part
	Proportion	0,43	0,22	0,1	0,08	Proportion	0,85	0,07	0,03	0,02	
	Principal Component Loadings from Correlation Matrix					Principal Component Loadings from Correlation Matrix					
	CB28	0,19	0,72	0,53	0,03	CB28	0,87	0,11	0,47	-0,01	
	HCB	0,42	0,64	-0,4	-0,01	HCB	0,91	0,2	-0,09	0,3	
	aHCH	0,5	0,55	-0,41	-0,3	aHCH	0,78	0,58	-0,16	-0,11	
	gHCH	0,8	0,44	-0,11	-0,25	gHCH	0,85	0,47	-0,02	-0,19	
	CB180	0,59	0,24	-0,05	0,57	CB180	0,93	-0,26	-0,1	-0,19	
	CB101	0,8	-0,11	0,16	-0,21	CB101	0,98	-0,13	0,12	0,07	
	CB118	0,75	-0,48	0,13	-0,32	CB118	0,94	-0,14	-0,02	0,07	
	CB138	0,87	-0,44	0,1	0,1	CB138	0,98	-0,09	-0,11	0,07	
	CB153	0,82	-0,5	0,06	0,1	CB153	0,92	-0,29	-0,07	-0,2	
	CB52	0,35	0,65	0,58	-0,22	CB52	0,95	-0,01	0,28	-0,03	
	4,4'DDE	0,79	-0,14	0,23	0,42	4,4'DDE	0,97	-0,04	-0,06	0,12	
	4,4'DDD	0,64	0,33	-0,36	0,33	4,4'DDD	0,97	-0,04	-0,11	0,17	
	4,4'DDT	0,63	-0,41	-0,21	-0,33	4,4'DDT	0,96	-0,2	-0,11	-0,11	

Figure captions

Figure 1. Correlation between first standardized principal component scores (SPC) and content of lipids in the muscle tissue of Baltic herring (2003-2005).

Figure 2. Correlation between first standardized principal component scores (SPC) and content of lipids in the muscle tissue of Baltic herring caught in a) 2003, b) 2004, c(2005, d) Gulf of Riga, e) Gulf of Finland West, f) Gulf of Finland East.

Legend of charts is identical with Figure 1.

Figure 3. Correlation between means of first standardized principal component scores (SPC) and means of content of lipids in the muscle tissue of Baltic herring.

BIOACCUMULATION TEST OF PERSISTENT ORGANIC POLLUTANTS IN *EISENIA FETIDA*: CHEMICAL ANALYSIS ISSUES

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Abstract:

Bioaccumulation of pollutants in earthworms must be seriously considered in ecological risk assessment, because it may result to toxic effects for earthworms and to biomagnification of food chains. Therefore, OECD bioaccumulation test guideline was prepared. However, we think that there are still some issues which are worth to consider when measuring the bioaccumulation of POPs in earthworms. Using the results gathered (let's say by the way) throughout our bioaccumulation experiments with spiked soils, *Eisenia fetida* and GC/MS analysis, we have compiled few recommendations. Firstly, it is necessary to control the soil spiking: (1) analyze spiking solution, (2) check real soil concentrations after spiking and contamination homogeneity, and (3) adjust moisture loss during spiking. We suggest here a procedure how to do these. Using described approach the variability of POPs distribution in the experimental soil was kept below 10%. When analyzing POPs in exposed *Eisenia fetida* it is necessary to know (1) variability and (2) background concentrations in worms. We performed 10 independent replicates of the bioaccumulation test and we found RSD 21%, 26%, 19%, 12%, and 30% for the accumulated concentrations of phenanthrene, pyrene, PCB 153, lindane, and DDT respectively. This is relatively high and it suggests that more than 3 replicates (as recommended in the new OECD guideline) should be used definitely. In worms from the control soil, we found some POPs which never exceeded 0.8 $\mu g/g_{dw}$. And finally, all necessary controls of recovery must run in analysis of both worms and soil. Cca 1/3 total loss of analytes during worms extraction and clean-up was mainly (70-90%) caused by nitrogen blow-down steps. It is also recommended to check the matrix effect on the analytical response.

Key-words: persistent organic pollutants, soils, artificial soils, bioavailability, bioaccumulation, *Eisenia fetida*, aging

Introduction:

Bioavailability is the key factor in soil ecotoxicology. A lot of chemical and biological methods have been developed for its assessment (Reid et al., 2000; Lanno et al., 2004). Although biological methods have some limitations, they are necessary because only they provide us the information about bioavailability itself without need of extrapolations and correlations which are required by chemical methods. Bioaccumulation in earthworms is a good example of the direct biological methods. It may result to toxic effects for earthworms and to biomagnification of food chain and it must be considered seriously in the ecological risk assessment. Therefore this task is frequently discussed (Jager et al., 2005) and an OECD bioaccumulation test guideline is finishing these days (OECD, 2005).

However, we think that there are still some issues which are worth to consider when measuring the bioaccumulation of persistent organic pollutants (POPs) in earthworms: i) the question of the right method of the soil spiking with POPs and how to control it (analysis of the spiking solution, moisture loss replenishment, real soil concentration check after spiking, assurance contamination homogeneity); ii) POPs in exposed *Eisenia fetida* from the viewpoint of the background concentrations in worms and variability of the internal body concentration of POPs; iii) the loss of contaminants during extraction and clean-up. At this paper, these issues are discussed using the results gathered throughout our bioaccumulation experiments with spiked soils, *Eisenia fetida* and GC/MS analysis.

Materials and Methods:

The spiking solution was prepared to contaminate 2 kg of soils. The target concentration was 10 mg/kg dry soil for phenanthrene and pyrene and 1 mg/kg dry soil for lindane, p,p´-DDT and PCB 153. Chemicals were dissolved in acetone and the spiking solution was analyzed with GC/MS after 200 x dillution and addition of internal standards (terphenyl and PCB 121).

Grassland soil with TOC of 5.6% was spiked using the „bowl method“ described by Doick et al. (2003). Briefly, soil (2 kg) was divided to four parts, spiking solution was added to the first one and mixed well with stainless-steel spoon for 5 min in stainless-steel bowl. There was control bowl with the same amount of soil to check the water loss. After the evaporation of acetone, lost water was added to the both bowls and these two portions of soil were well mixed together for 5 min. Then, the third and fourth parts were mixed the same way with the contaminated soil.

Concentration of added contaminants and homogeneity of contamination were checked by taking 5 independent samples from the soil. They were extracted in boiling DCM by Randall extraction on Velp Scientifica extractor SER 148 after addition of recovery standards (D-phenanthrene, D-pyrene, PCB 30, and PCB 180). Extracts were cleaned on silica-gel columns and measured with GC/MS after addition of internal standards (terphenyl and PCB 121).

Ten groups of ten earthworms *Eisenia fetida* from culture were extracted and analyzed to assess background concentrations. Extraction and analysis were performed the same way as for soil, but gel permeation chromatography (GPC) was included before celan-up on silica gel columns to remove lipids from extracts.

Bioaccumulation test with the spiked soil was performed. Ten groups of ten earthworms were exposed in 200 g soil (moistened to 50% WHC) in glass jars for 10 days. After the exposure time the groups of earthworms were analyzed the same way as the groups of earthworms assessed for background concentrations.

Loss of analytes during extraction and clean-up steps was monitored with series of control extracts with recovery standards (D-phenanthrene and PCB-30), which were added before each step of analysis - extraction, evaporation and chloroform addition, GPC, clean-up on silica-gel columns, and blow-down under nitrogen. The samples were analyzed again with GC/MS.

Results and Discussion:

The real concentrations in the spiking solution were higher than the targeted concentrations (**Table 1**, the first and second row). This could be caused by combined effects of inaccurate weighting of low amounts, evaporation of solvent during manipulation and measuring towards calibration from bought mixed standards. Only for p,p´-DDT the concentration was lower, probably caused by wrong calibration of this analyte. Anyway, measured concentrations must be considered for all next calculation instead of theoretical (targeted) concentrations.

Table 1. Spiking of grassland soil (TOC 5.6%) considering the target and measured concentrations of spiking solution and soil, recovery and loss of contaminants during spiking

	PHE	**PYR**	**LIN**	**p,p´-DDT**	**PCB 153**
Target concentration in the spiking solution (µg/ml)	500	500	50	50	50
Measured concentration in the spiking solution (µg/ml)	1,320	1,241	90	35	66
Target concentration in the soil (µg/g)	10	10	1	1	1
Concentration in the soil expected from the measured concentration in the spiking solution (µg/g)	26.4	24.8	1.8	0.7	1.3
Measured concentration in the soil (µg/g)	10.6	7.9	0.6	0.4	0.8
Coefficients of variance (n = 5)	4%	3%	11%	12%	8%
Recovery	55%		77%		
Concentration in the soil – recovery adjusted (µg/g)	19.2	14.3	0.8	0.5	1.1
Contaminants loss during spiking – recovery adjusted	27%	42%	56%	27%	20%

The water loss during spiking was significant. Using checks by weighting, 4 hours were needed to evaporate acetone in the fume-hood. During this period, 15 – 30 ml of water was lost from 1 kg wet soil. This amount must be added to the soil before its use in the bioaccumulation test.

The real concentrations in soil after spiking were also different than expected from the measured concentrations of the spiking solution (**Table 1**, rows 3 - 9). The difference between these concentrations was influenced by recovery, which was 55% for PAHs and 77% for chlorinated POPs. After recalculation for recovery, the concentrations were still lower than expected from spiking solutions. This was probably caused by loss of contaminants during spiking. Some authors showed lower losses (12 - 23%) but they spiked 20 or 200 g while we did 2 kg, which might be the reason (Doick et al., 2003; Sverdrup et al., 2002).

The homogeneity of contamination was satisfactory in our study - coefficients of variance of repeated sampling from the 2 kg soil were 3 - 12%. This confirms spiking method of Doick et al. (2003) as appropriate to provide homogenously contaminated larger amount of soil for bioaccumulation studies with earthworms.

Background concentrations in earthworms from the culture were low. Many contaminants were below detection limits (**Table 2**). The most important chlorinated contaminant was PCB 153 (0.03 $\mu g/g_{dw}$), non-chlorinated contaminants were naphtalene (0.37 $\mu g/g_{dw}$), phenantrene (0.47 $\mu g/g_{dw}$) and pyrene (0.72 $\mu g/g_{dw}$). However, the knowledge of background concentrations is necessary especially if the study aim is to measure bioaccumulation in soil with concentrations close to enviromental levels.

Table 2. Backround concentrations in *E. fetida* from the culture used in the experiment (µg/g_{dw})

Naphtalene	0.37
Acenaphtylene	0.01
Acenaphtene	0.03
Fluorene	0.06
Phenantrene	0.47
Fluorantene	0.10
Pyrene	0.72
Chrysene	0.01
Suma 16 PAHs	1.77
PCB 153	0.03
PeCB	0.01
alfa-HCH	0.01

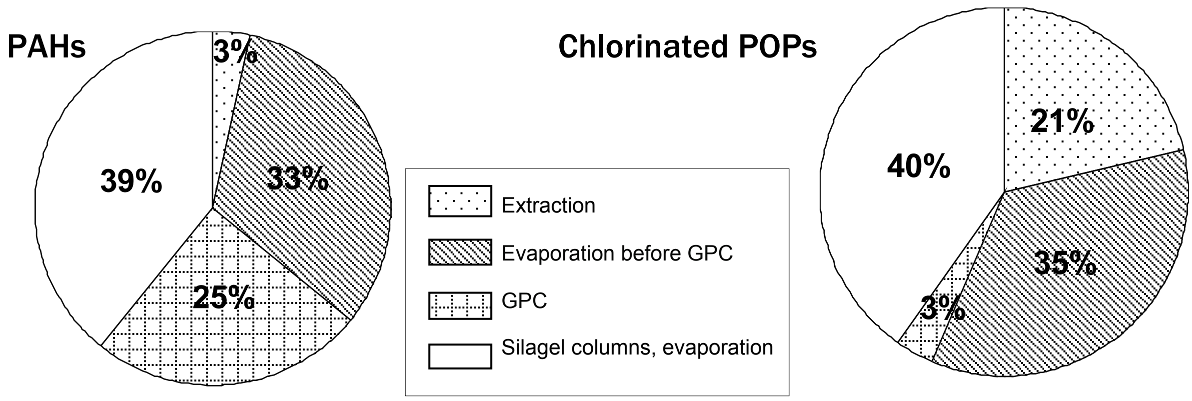
Table 3. Concentrations of tested contaminants in *E. fetida* (µg/g_{dw}) exposed in spiked grassland soil

Phenantrene	40.39 ± 8.38
Pyrene	56.74 ± 14.49
γ-HCH - Lindane	2.80 ± 0.32
p,p'-DDE	0.22 ± 0.05
p,p'-DDD	0.44 ± 0.09
p,p'-DDT	1.29 ± 0.38
PCB 153	5.96 ± 1.12

Exposed earthworms *Eisenia fetida* in contaminated soil showed significantly higher concentrations than earthworms from the culture (**Table 3**). Although 10 replicates were performed, measured concentrations in earthworms revealed high **coefficients of variance** (21%, 26%, 19%, 12%, and 30% for phenanthrene, pyrene, PCB 153, lindane, and DDT, respectively). This might indicate that more than 3 replicates (OECD, 2005) are needed in POPs bioaccumulation tests with earthworms.

The **loss of analytes** during extraction and clean-up steps is illustrated in the **Figure 1**. Totally, recovery was only 65% for PAHs (measured as D-phenanthrene) and 77% for chlorinated POPs (measured as PCB 30). The major loss was observed in two steps where samples were blown-down under nitrogen stream in the fume-hood.

Figure 1. The loss of analytes during extraction and clean-up. The total recovery for PAHs was 65%, for chlorinated POPs 77%.



Conclusions:

The measured concentrations in the spiking solution and the measured concentrations in the soil differed from the targeted concentrations. Question remains, what could be the reason. Spiking method according to Doick et al. (2003) provided homogenous contamination of soil although relatively large amount of soil was spiked (2 kg). In bioaccumulation studies, earthworms from the culture should be checked time to time to prevent the background contamination. However, POPs in our culture never exceeded negligible 0.8 $\mu g/g_{dw}$ in *E. fetida*. Variability of POPs concentrations in the exposed earthworms seems to be high. Relatively high number of replicates (10) still revealed variability from 12 to 30%. We suggest five replicates as a compromise between practicability and accuracy of the test. Recovery must be carefully controlled in the bioaccumulation tests with POPs, especially blow-down under nitrogen in the fume-hood.

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