

7TH INTERNATIONAL HCH AND PESTICIDES FORUM

**«TOWARDS THE ESTABLISHMENT OF AN OBSOLETE
POPS/PESTICIDES STOCKPILE FUND FOR CENTRAL
AND EASTERN EUROPEAN COUNTRIES (CEEC) AND
NEW INDEPENDENT STATES (NIS)»**

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Organizing Committee, International Advisory Committee and the International Advisory Committee of the 7th International HCH and Pesticides Forum would like to thank all people and institutions for the excellent cooperation during the preparation work of the Forum.

We warmly appreciate all sponsors – without your help the Forum would not have been possible.

The Forum and this book are the result of joint efforts of many people involved in the problems of obsolete pesticides which are spread all over the world.

We will continue our efforts towards sustainable solutions for our environment

Great thanks to all of you!!!

We specially thank to Ms. Ebtesam Elbestawy, Ms. Nanna Schulz, and Ms. Iryna Pidlisnyuk who have been working editing the contributions of the authors.

FOREWORD

The 7th International HCH and Pesticides Forum in Kyiv has created a new international movement and commitment towards solutions for the problems of obsolete pesticides in the region of Central and Eastern Europe, Caucasus and Central Asia. The book documents this common vision towards a real and feasible solution.

The Book has two sections and attachment.

First official section represents official documents from the opening ceremony, the Roundtable's results held in the Ukrainian Parliament and the Kyiv Declaration adopted at the Roundtable.

At section 2 all presentations of technical sessions, poster presentations and submitted papers by authors that have not been able to come to Kyiv are summarized.

Attachment represents data about authors and participants of the Forum.

We hope this Book will serve as important piece of information for public, experts and governmental officials towards improvement the state of environment.

We are sure that more and more parties will join us in our common works and goals to eliminate obsolete pesticides in the region.

*Bram de Borst, Dmytro O. Melnychuk, Valentyna V. Pilisnyuk,
Tatyana R. Stefanovska, Konstantin Terytze, John Vijgen*

WELCOME SPEECH

Valentina Pidlisnyuk

*Head of the Organizing Committee, Deputy Chair of the International Advisory Board
at the 7th International HCH&Pesticides Forum, professor*

Dear Honorary Guests, dear participants, ladies and gentlemen!

On behalf of the Organizing Committee and International Advisory Board I would like to open the 7th International HCH& Pesticides Forum and to greet all of you in Ukrainian capital Kyiv, which is particularly beautiful now at early summer.

This Forum entitled «Towards the establishment an obsolete POPs/pesticides stockpiles fund for Central and Eastern European countries, Caucasus Republic and middle Asians Republics» has a goal to draw an international attention to one of the biggest international environmental problem stemming from the accumulation of obsolete pesticides in storages and their harmful effects on human health and the environment. The Forum would like to strengthen an international awareness regarding crisis situation with obsolete pesticides stockpiles and to address the problems to political decision makers.

We would like to thank to the Ukrainian Parliament, Ukrainian Governmental and National Agricultural University of Ukraine for full support they expressed while at the preparation process. We greatly thank s to our sponsors: Danish Environmental Protection Agency, European Crop Protection Association, Federal Environmental Agency of Germany, Ministry of Environment of Finland, Swiss Agency for Development Cooperation, Department for Environmental Food and Rural Affairs at Defra, and European Commission. Also we thank to sponsors for travel support: UNEP-International Environmental Technology Centre, Japan and Swedish Environmental Protect Agency. The Forum is a result of joint efforts and supports of many people involved from Ukraine and abroad and it is my pleasure to thank all of you for assistant.

Today 137 governmental officials, experts, scientists, member of NGOs and representative persons from international and intergovernmental organizations from 34 countries and 47 Ukrainian participants meet in Kyiv having goal to discuss the problems of obsolete pesticides and to propose ways for solution. The importance of the Forum is confirmed by it's official registration as a side event of the 5th Pan-European Ministerial Conference «Environment for Europe» and by letters of support we received from over 20 countries.

5th of June is a special day for environmentalists: it is a World Environmental Day. It was first declared in 1972 by United Nations and since that time marked as a major event for ecological calendar. The 5th of June is a Day when people across the world join their efforts for nature protection and preservation, and doing practical contributions to make our planet sustainable. It sounds symbolic that we are opening 7th International Forum particularly that day.

We all at the Organizing Committee and International Advisory Committee hope that two and half days of work will be very fruitful and productive for you as Forum's participants. We believe that activities included into agenda: reports, presentations, discussions, as well as Round table in Ukrainian Parliament, field trip and Phytoremediation workshop will make a significant contribution for solving the problems of Obsolete pesticides in the region of Eastern and Central Europe, Caucasus Republic and Middle Asian Republics and be fully supported by responsible European organizations.

On behalf of Organizing Committee and International Advisory Committee I wish to all of you an effective work, fruitful discussions and enjoyable conversations.

Thank your very much for your attention!

OPENING SPEECH

Ivan Zaetz

*Deputy Head of the Committee on Environmental Policy, Nature Resources
Utilization and Elimination of the Consequences of Chernobyl Catastrophe of the Ukrainian Parliament*

Dear participants of 7th HCH and Pesticide Forum!
Dear guests and friends!

On behalf of members of the Committee on Environmental Policy, Nature Resources, Utilization and Elimination of the Consequences of Chernobyl Catastrophe of the Ukrainian Parliament I want to congratulate you on Ukrainian land and to wish a productive and successful work during three days of 7th International Forum.

The conducting a Forum in Kyiv, Ukraine is an event of great importance to our country as it will promote attracting an attention of government representatives, public, experts, members of NGO's to an issue of procession and utilization of unauthorized pesticides and to a necessity of elaboration of conciliation program of actions within Central and Eastern European countries, Caucus Republics and Middle Asia countries.

Ukraine has inherited a problem of unauthorized pesticides from Soviet Union times, when it was highly agrarian developed and was considered to be the major supplier of agricultural products to the whole Soviet Union. Agriculture was developing that time in an intensive way with a wide use of pesticides and chemicals. For example, during 70's and 80's in last century some 3-4 kg of pesticides were used per 1 hectare, and the majority of these pesticides were put down to an unauthorized pesticides sites later on.

A great number of pesticides were accumulated in warehouses at the same exact time. Their quantity ranges between 13,000 and 20,000 tones, and they are kept in inappropriate conditions. It results in falling of toxic compounds and products of their decomposition into environment, including water streams, air, and agricultural products. The problem arises also owing to the fact that a lot of documentation has been often lost after a long time of preservation, as a result what were kept, couldn't be identified. Long-lasting storing has promoted chemical transformations and sometimes even reactions with a creation of new unknown substances.

The situation got worse in the 90's, when Ukraine lost control over supply of the imported chemicals due to disintegration of State Agrochemical Service's structure. Great number of chemicals had been imported to the country, that later on were found unauthorized and toxic. We don't have reliable and detailed information about the presence of pesticides; monitoring of underground water, soil, and agricultural products around places of their storages; additionally preservation is nearly absent, people are not educated and accustomed with an appropriate behavior with pesticides and poison chemicals, and usually don't know about their harmful impact on health.

Ukraine among more than 90 other countries signed Stockholm Convention about persistent organic pollutants (among them are 12 the most harmful substances) in May, 2001. Now the problems of comparison analysis between Stockholm Convention content and Ukrainian active legislation, consideration of ratification, calculations of possible economic consequences are posed. Ukraine has to enforce the process of ratification which will open new possibilities for the solution of unused banned pesticides in Ukraine.

I would like to mention that Forum has been scheduled in Ukraine and that fact one more time stresses that country has a leading role in environmental issues. We are open for discussion with international community regarding ways for solving problems of Obsolete Pesticides. Ukraine would like to propose to unify approach to the problem and is ready to have a contact with international donors and organizations for promoting projects in Ukraine focused on utilization an existed huge number of obsolete pesticides stockpiles and sites we have across Ukraine.

Summarizing I would like to wish you a productive and fruitful work and discussion today and tomorrow morning and to invite you to Ukrainian Parliament for Round Table tomorrow afternoon.

Thank you for attention.

OVERVIEW OF ROUNDTABLE AND FINAL SESSION ON POLITICAL DECLARATIONS IN THE UKRAINIAN PARLIAMENT ON 6TH OF JUNE 2003

Presided by Gennadiy Rudenko, Ivan Zayets and Yuri Solomatin

*Chair, Vice-Chair and Secretary of the Committee on Environmental Policy,
Nature Resources, Utilization and Elimination the Consequences of
Chernobyl Catastrophe at the Ukrainian Parliament*

Organisation	Representative	Documents available
Ukrainian Parliament	Gennadiy Rudenko	Included in this section
Ukrainian Parliament	Ivan Zayets	See in Official Opening
Ukrainian Parliament	Yuri Solomatin	–
EU Delegation in Ukraine	Norbert Jousten	Included in this section
AFIDE	Ms. Archalus Tcheknavorian	Included in this section
Basel Convention Regional Centre Bratislava	Ms. Dana Lapesova	Included in this section
FAO	Mark Davis	See Kyiv declaration and overview of support letters
GEF	Andrea Merla	–
Nordic Environmental Finance Corporation	Ahmadzai Husamuddin	–
Syngenta Foundation for Sustainable Agriculture	Jost Frei	See Kyiv declaration and overview of support letters
UNEP Chemicals	Garislav Skholenok	Included in this section
Armenian Government	Ms. Anahit Aleksandryan	See Kyiv declaration and overview of support letters
Bulgarian Government	Ms. Valentina Vassileva	See Kyiv declaration and overview of support letters
Czech Government	Ivan Holoubek	See Kyiv declaration and overview of support letters
Danish Government	Ms. Mikala Klint	See Kyiv declaration and overview of support letters
Georgian Government	Alverd B. Chankseliani	See Kyiv declaration and overview of support letters
German Government	Konstantin Terytze	–
Latvian Government	Ilgonis Straus	See Kyiv declaration and overview of support letters
Moldavian Government	Stefan Stasiev	See Kyiv declaration and overview of support letters
Swiss Government	Urs Kluser	See Kyiv declaration and overview of support letters
IHPA/Tauw Milieu	Bram de Borst	Reading of final Declaration. See Kyiv declaration and overview of support letters
IHPA	John Vijgen	Closing remarks Included in this section
Organizing Committee of 7th International Forum	Ms.Valentina Pidlisnyuk	See in Official Opening

INTRODUCTION

Gennadiy Rudenko

Chairman of the Committee on Environmental Policy, Nature Resources Utilization and Elimination of the Consequences of the Chernobyl Catastrophe of the Ukrainian Parliament

Dear participants of the Forum!

Let me greet you on behalf of the highest Ukrainian legislative body – Ukrainian Parliament. This Forum is held as an accompanied event for 5th European Ministerial Conference, which has recently finished its work in Kyiv. Within the framework of this conference we held a session with the participation of members of European Parliament, representatives of Ecological Departments and NGOs in the same hall. The idea of the conduction of the 7th International HCH & Pesticides Forum and its importance in the context of European Ecological process gained absolute approval in this session.

The Forum is held with the support of the Committee on Environmental Policy Nature Resource Utilization and Elimination the Consequences of Chernobyl Catastrophe, and conduction of the roundtable is to the committee's official draft.

A fact that Forum is conducted in Kyiv and there is a great international involvement in it says about its singularity and about Ukraine's active position in European work towards solution of the persistent organic pollutant's problem.

Let me briefly tell about Committee's functions and structure. The main tasks of Committee are:

- work on bills about environmental conservation and preservation;
- study practices of implementation and execution of passed laws;
- participation in parliament control over execution of Ukrainian laws;
- realization of international cooperation on questions that concern work of the Committee.

The structure of committee includes 4 subcommittees on questions of:

- ecological policy and nature use;
- ecological and technical security, and emergency situations;
- development of newest ecologically safe technology;
- overcoming of the consequences of Chernobyl catastrophe.

Our Committee has always paid great attention to the problem of behavior of toxic waste. The problem of pesticides is complex. It includes ecological, economic and social issues and therefore it should be considered from the point of sustainable development. A great amount of unused banned for use pesticides (app. 20,000 tons) that were left from Soviet times, are laid up in Ukraine now.

The state of pesticides' conservation and utilization doesn't meet standards of Ukrainian Law «About Pesticides and Agrochemicals», and doesn't provide population's health and environmental security. Therefore there is a need for taking emergent actions for improvement of this issue.

Ukrainian laws about pesticide issue are:

- law «About Pesticides and Agrochemicals» (1995);
- national program of behavior with toxic waste (2000).

Ukraine has also signed Stockholm Convention on persistent organic pollutants (2001).

Some of the pesticides belong to persistent organic pollutants, which need special approach elimination.

Ukraine is in the process of spadework for ratification of Stockholm Convention now. Its ratification will open new possibilities for the solution of unused banned problem.

I will stop briefly on a social aspect of the problem. People know nearly nothing about the thread of this waste. The access to information on questions concerning pesticides and public participation in decision-making process is very important. I want to inform our foreign guests that Ukraine was the second among the European countries to ratify the Aarhus Convention «On access to information, public participation in decision-making process and access to justice on environmental issues». Changes in some of the Ukrainian laws were made, due to ratification of the Convention. It is also a good foundation to pesticides' problem solution.

Economic issue of this problem is important. At a present time there are several techniques of utilization of unused banned pesticides: packing in containers, incineration and pyrolysis. It's necessary to choose the most efficient and ecologically safe one for Ukraine.

For current year it is planned to give 10 million grn for the National program of behavior with toxic waste from National Budget. But it is not enough. We hope for international cooperation on this issue. Creation of a Fund for utilization of unused banned pesticides' warehouses in Central and Eastern European Countries, Caucasus Republics and Middle Asia is of great importance.

What questions will be discussed on today's roundtable? They are:

- generalization of unused banned pesticides' situation in Ukraine and other countries;
- discussion of the ways for solution of this problem;
- discussion of Kyiv Declaration About Fund for utilization of unused banned pesticides' warehouses in Central and Eastern European Countries.

Thank you for your attention.

POSSIBLE EUROPEAN UNION ASSISTANCE FOR UKRAINE

Norbert Jousten

*Head of the European Commission
Delegation in Kiev*

Background

Stocks of obsolete pesticides are widespread in the world and form a severe threat of irreversible damage to human health and the environment. We do not have much information on Ukraine and NIS, but we probably can compare with what happened and is happening in the EU acceding countries. These countries have the obligation to transpose and implement the *acquis*. Unfortunately, for many years, most of these countries did not recognise the problem. They now have very short time to adapt. They could use EU structural funds for this purpose.

Possible approaches and EU Funding:

Neither the Commission nor the EU Parliament are in favour of creating a specific fund, but rather to use existing tools (i.e. Structural funds in the new Member States, Phare / ISPA in candidate countries and TA programmes in the NIS).

Archalus Tcheknavorian

AFIDE, Vienna, Austria

Ladies and gentlemen,

Let me to start with thanking the organizers of this conference with a very interesting and well-chosen topic, bringing together such a high level audience from science, industry and governments. I wish also in this connection to thank the government of Ukraine for their generosity, hospitality and capable chairmanship, which has contributed to the success of the meeting in archiving its objective and goal. I know, how difficult it is to organize such technical meeting, with such a contrast topic. I have to congratulate MR. JOHN VIJGEN for his energy, devotion and persuasion for making possible the conference and for us to participate, not only to contribute but also an opportunity to update our knowledge or to learn the new and divers technological advancements for handling the pesticides and their safe use. Ladies and gentlemen allow me in this prestigious parliament and in front of the parliamentarians to present to you my experience in sustainable development and its impact to the developing countries effort in their development. After 30 years of service in UNIDO and UN, as technical officer, managing director for environment and

The main possibility in Ukraine and in other NIS is the TACIS programme. The TACIS programme can assist in capacity building for the development of waste management plans or investment support for safe disposal facilities.

This can be done through the TACIS National Programme. The «Local development in selected municipalities» section of the Indicative Programme 2004- 2006 includes waste management.

Some other support can also be given through a small project programme facility (Bistro).

In Ukraine, TACIS may possibly help financing establishing inventories in selected areas. In the framework of de-monopolisation and privatisation of municipal services, with interested IFIs, TACIS may also prepare the procurement of management contracts in order to outsource the provision of municipal services to private enterprises.

If the Ukrainian government wants more assistance, it has to clearly put environment as a priority in the next Indicative Programme (2007 – 2009).

industrial sectors, as senior adviser for environment for Europe and CIS countries (UNDP) and now as president of a UN NGO, AFIDE (Association of Former Industrial and Development Experts) of UN, as well as enjoying a special status with ECOSOC) a non-profit organisation which has been created in 1997 with the aim to assist the developing countries and countries with economies in transition, I have come to the following conclusion during my 30 years of experience on development issues, which I would like to share with you:

It is a say, join UN and see the world and make friends around the world I fully agree to it, and I am grateful to UN, however it has not always been an enjoyable task neither the journeys nor the work. It has been difficult to travel in almost 165 countries of the world, however with the privilege to review and understand the countries development pattern, the successes, failures and problems. I always noted with every government, that the government's major dilemma was to make the choice between so many needs, actions, policies and finally projects and institutions to execute. This process was the most difficult period of our job by assisting the member states in their identification process and thereafter formulation of projects, activities etc. for realisation of their views and policies. It is important to be said that in 1974 at UNIDO conference in LIMA / PERU, the total world output of the

developing countries was in the magnitude of 8%, a goal was set up to reach 25 % share of world markets for developing countries by the year 2000 with the assistance of UNIDO these declaration is known as LIMA declaration. I can testify that during the last 25 years many countries advanced from a low level economical and industrial to a higher level economical performance by the year 2000 or before, however only a handful countries could sustain their development level, and others they either lost or never achieved. From today's perspective could be said that all those countries which had integrated sustainable development as their strategy while advancing their economical, technological, environmental and human resource development, they have succeeded and they are enjoying much higher economical performance as 1974, all those countries which were only driven for development without considering its sustainability have reduced their economical performance in addition to many industrial, technological and environmental disasters which they have to address now. However it is never late to

address and to take corrective measures to overcome shortcomings but never can it be acceptable to ignore or to keep silent, because the question is arising from this behaviour, who should be blamed, or who will pay for it? If we will not take care today, then we are going to leave our created problems for the next generation to come. I believe Mr. JOHN VIJGEN believes you all participants believe and that is why we are here, we have to do it ourselves, therefore let us join hands to make these recommendations, and the expression of support expressed by advanced countries, financial institutions, NGO's and industry during this meeting, responding to the desire expressed by the host government and other Central European and EECCA Countries, and developing countries for a change in their development pattern to become reality, because the people of all the countries have the right to live in dignity and with human respect. AFIDE will fully support the outcome of this meeting and contribute according to its mandate including the availability of human and financial resources. Thank you.

THE PROBLEM OF STOCKPILES OF OBSOLETE/BANNED PESTICIDES IN THE CIS COUNTRIES

Garislav Shkolenok

*UNEP Chemicals, IEH, 11-13,
ch. des Anémones, CH-1219
Châtelaine, Geneva, Switzerland*

Thousands of tons of obsolete/banned pesticides, including POPs pesticides, are being scattered across the countries of the Commonwealth of Independent States (CIS). In Russia alone, over 25,000 tons are stored in numerous locations. Ukraine takes the second place in the region with its 19,000 tons. Large amounts are also possessed by Kazakhstan and Uzbekistan. A general problem is poor packaging and storage conditions, resulting in releases of these harmful chemicals into the environment. Evidently, the problem of stockpiles of obsolete/banned pesticides is very crucial for the region due to significant risks posed to human health and the environment. Moreover, in terms of its scale and consequences, the threat of the stockpiles, which grows with time, is comparable with that one caused by radioactive substances, and, in certain countries, even exceeds the latter.

As up to 40-50% of the total amounts of stockpiles are presented by unidentified mixtures of pesticide preparations, the government authorities concerned clearly recognize that the proper approach to the management of

such pesticides is their destruction/elimination in the environmentally sound manner. To implement this task, the full inventory of stockpiles needs to be developed in each country. For this purpose, various activities were initiated with support from UNEP Chemicals and many member-countries of the Arctic Council. For example, the pilot UNEP/US EPA project for developing inventories in four regions of Russia, UNEP Chemicals studies on estimate inventories in Kazakhstan and Uzbekistan, joint Belarus-Denmark and Ukraine-Denmark projects, and, finally, the ACAP project on Environmentally Sound Management of Stocks of Obsolete Pesticides in the Russian Federation.

The Subregional Workshop on Inventories of Stockpiles of Obsolete Pesticides was organized in Krasnodar, Russia, from 26-28 May 2003 within the framework of the joint UNEP/Russia project on Strengthening National Chemicals Management in CIS Countries. Officials and experts from agriculture, natural resources/environmental protection and health ministries attended the meeting. The main objective was to review the status of the problem of stockpiles in the region and to discuss ways and means for its solution. More specifically, the workshop was aimed to agree on a common approach to developing inventories of such stockpiles and, as the first step, to discuss and adopt the Technical Guidance on Developing an Inventory, Identification, Collection and Storage of Obsolete and Banned Pesticides, which was prepared by Russian experts. This initiative was welcomed due to both the common legacy and similar economic conditions as related to this problem in all CIS countries,

It was concluded that insufficient financial and human resources, and poor technical basis would not allow the CIS countries to develop the full inventories of stockpiles without financial and technical support from international organizations and donor countries. In this respect, the importance of international efforts focused on the implementation of the Stockholm Convention on Persistent Organic Pollutants should not be underestimated. Of particular importance is the POPs inventory work planned under the GEF funded country projects for developing National Implementation Plans (NIPs) for the Stockholm Convention. Such work, for example, has started by UNEP Chemicals and Ukraine quite successfully. The urgency of ratification or accession to the Stockholm Convention and Rotterdam Convention on the Prior Informed Consent for Certain Hazardous Chemicals and Pesticides in the International Trade was also unanimously recognized.

Attention was drawn to the necessity of improving national legislation with regard to the safe handling of pesticides at all stages of their life, with due consideration for international guidance and recommendations. It was agreed upon that the CIS countries should strengthen control over the illegal imports/exports of obsolete and unregistered pesticides, using the mechanisms of the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal as well as the Prior Informed Consent (PIC) Procedure of the Rotterdam Convention. It was also recommended that the CIS countries should implement inter-state harmonization of requirements for pesticides registration and to develop preventive measures aimed to exclude the piling-up of the removed counterfeited preparations.

UNEP was requested to consider opportunities for developing a regional programme on environmentally sound management of stockpiles of obsolete pesticides in

the CIS countries and to assist in identifying interested donors.

With this in view, UNEP and the Governments of CIS countries were encouraged to participate in the 7th International HCH and Pesticides Forum, Kiev, 5-7 June 2003 and to work together with the other stakeholders and support the establishment of an Obsolete POPs/Pesticides Stockpile Fund/Project/Programme for Central and Eastern European Countries (CEEC) and New Independent States (NIS). This is urgently needed to relieve the region of the obsolete/banned pesticides problem.

In addition, participants in the Krasnodar workshop commended the EU Commission on its letter of 26 March 2003, where Director General of the Directorate General Environment declared to share the opinion that obsolete pesticides pose a problem, in particular in CEEC/NIS countries, and also encouraged the CEEC/NIS countries to make use of the EU funding possibilities that existed. In order to make proper use of these funding possibilities, UNEP and the International HCH & Pesticides Association were requested to help the CIS countries with the preparation of proposals for inventories and the following implementation works, to the EU Commission. This applies in a similar way to GEF and other donor organisations, in order to bring forward the necessary progress for concrete solutions.

The 7th International HCH and Pesticides Forum in Kiev hosted by the Government of Ukraine, National Agricultural University and Sustainable Development and Ecological Research Centre provides an excellent opportunity for exploring urgent practical measures in this subject area. This Forum is going to be a real milestone on the way of promotion of regional and international co-operation, which will help this region to solve the problem of stockpiles of obsolete/banned pesticides.

Dana Lapešová

Basel Convention Regional, Centre Bratislava

Dear Ukrainian Parliament members, ladies and gentleman, dear colleagues.

The Strategic plan for the implementation of the Basel Convention to 2010 emphasized the necessity of managing the hazardous wastes in an environmentally sound manner including the stockpiles of such wastes and the importance of building public and private multistakeholders partnership to achieve this goal.

The Basel Convention Regional Centres are one of the key delivery mechanisms to implement this Strategic plan at the regional level.

As we know stocks of obsolete pesticides are widespread and present severe threats to human health. We know also that the actual size of the problem is unknown.

There is insufficient awareness at public level.

There is a lack of proper facilities to dispose or destroy the stockpiles of pesticides.

There is a lack of financial resources.

From this point of view we consider as important and urgent:

Develop and successful implement the national inventories system of the stockpiles of pesticides with a view to their timely disposal.

Establish regional or subregional mechanism to improve and consolidate cooperation among countries.

Create public awareness and training programmes.

Create public and private partnership including the

involvement of the civil society and ensure access to information to all concerned.

Develop resource mobilisation strategy and create regional strategy on environmentally sound management on stock obsolete pesticides.

Finally,

I would like to express a strong support of the Secretariat of the Basel Convention through Basel Convention

Regional Centre in Bratislava to all activities leading the countries of the region to solve the pollution problems of pesticides and other POP chemicals and we keep to be active to support the countries in their activities to facilitate funding for national and regional activities.

Thank you to have a possibility to come here to Ukrainian Parliament which we can see as a strong political support to environmental activities, especially to solve the problem of stock obsolete pesticides.

CLOSING REMARKS

John Vijgen

International HCH & Pesticides Association

Let me summarize our impressions of the last 2 days:

The Ukrainian position on obsolete pesticides:

- We have seen a strong political commitment
- The issue is recognized as an important social and economic problem
- Work has commenced step-by-step and at present Ukraine has made a budget allocation of 9.4 Million Gryvna, being approximately 1.75 Million US Dollar for 2003
- We have seen joint-efforts by the ministries of Agricultural Policy and the Ministry for Environmental Protection
- Ukraine recommends a unified approach and a financing mechanism and a Programme of Action for Central Europe and EECCA is fully supported by the Ukrainian Parliament

Our impressions from the 7th Forum:

- We have seen the personal commitment from all participants – to share their knowledge – through presentations and posters and in the discussions
- We have seen the commitment until today of 22 Ministers of Environment throughout the larger European Region, Caucasus and the Central Asian States
- The commitment from international donors to see if we can move in a more result-oriented way
- The Global Environment Facility has offered to act as catalyst in the process

Technical issues which have been addressed:

- Monitoring and risk assessment (with impressive contributions from Ukraine)
- Waste management and in particular waste destruction techniques and the importance of public awareness and acceptance

- Sustainable use of pesticides (safety, reduction and waste prevention)
- Phytoremediation for pesticides contaminated soils with excellent teachers from US and Canada

Thanks to the Hosts and the warm Ukrainian hospitality:

- National Agricultural University of Ukraine
- Sustainable Development and Ecological Research Centre, Ukraine
- Federal Environment Agency, Germany
- Board of the International HCH & Pesticides Association

Thanks to the Sponsors and without their help we would not been able to gather here:

- Danish Environmental Protection Agency – Danish Cooperation for Environment in Eastern Europe (DANCEE)
- Department for Environment Food and Rural Affairs (Defra), United Kingdom
- European Commission, EuropeAid, Co-operation Office Europe, Caucasus, Central Asia,
- Thematic Support, Private Sector and Economic Reform
- European Crop Protection Association (ECPA)
- Federal Environment Agency of Germany (UBA)
- Ministry of Environment of Finland
- Swiss Agency for Development Cooperation, SDC, Switzerland

Thanks for the sponsors for travel support:

- UNEP-IETC, Japan
- Swedish EPA

Welcome:

To the Bulgarian government which is planning to host the 8th International HCH And Pesticides Forum in 2005 in Sofia

KYIV DECLARATION ON THE ESTABLISHMENT OF A POPS AND OBSOLETE PESTICIDES STOCKPILE PROGRAMME FOR CENTRAL AND EASTERN EUROPE, CAUCASUS AND CENTRAL ASIA COUNTRIES FOR THE ENVIRONMENTALLY SOUND MANAGEMENT OF UNWANTED STOCKS OF POPS AND OTHER OBSOLETE PESTICIDES

PREAMBLE

The 7th International HCH and Pesticides Forum was held in Kyiv, Ukraine, from 5 to 7 June 2003, at the National Agricultural University and was finalised at the Ukrainian Parliament, with the 150 participants. The Forum dealt with the continuing risk of damage to the environment and of harmful effects on human health caused by the environmentally unsound management of stocks of hazardous wastes, in particular obsolete pesticides and other unwanted persistent organic pollutants (POPs) and made strong efforts to work towards the establishment of a POPs and Obsolete Pesticides Stockpile Programme for Central European and EECCA Countries for the environmentally sound management of unwanted stocks of POPs and other obsolete pesticides. On the first day of the forum a draft declaration has been distributed to all participants with the request for comments. At the end of the first day a special Committee consisting of representatives of AFIDE, BCRC in Bratislava, Bulgarian Ministry of Environment and Water, Crop Life, DANCEE (not permanently), Dutch Ministry of Housing, Spatial Planning and the Environment, FAO, IHPA, Nordic Environmental Finance Corporation, Secretariat of the Basel Convention, Ukrainian Ministry of Ecology (former representative), UNEP Chemicals, UNIDO, US EPA (not permanently) all comments have been evaluated and the declaration was finalised for presentation in the Ukrainian Parliament. The declaration was presented on the second day in the Ukrainian Parliament, discussed, and necessary amendments were included. Finally, the declaration was endorsed by all participants of the Round Table in the Ukrainian Parliament.

We, the 150 participants (see Annex 1) of the 7th International HCH and Pesticides Forum,

Having met in Kyiv, Ukraine, from 5 to 7 June 2003;

Concerned about the continuing risk of damage to the environment and of harmful effects on human health caused by the environmentally unsound management of stocks of hazardous wastes, in particular obsolete pesticides and other unwanted persistent organic pollutants (POPs);

Having noted with grave concern that during the current ongoing transition period of Central European and EECCA Countries it has still not been possible to address the urgent and complex problem of deteriorating stocks of obsolete pesticides, in particular regarding the ownership of the wastes;

Committed to the principles of the Ministerial Basel Declaration on Environmentally Sound Management adopted on the occasion of the fifth meeting of the Conference of Parties to the Basel Convention and the tenth anniversary of the adoption of the Basel Convention in December 1999;

Also committed to the implementation of the Stockholm Convention on Persistent Organic Pollutants (POPs);

Reaffirming Principle 16 of the Rio Declaration on Environment and Development which states that national authorities should endeavour to promote the internalisation of environmental costs and the use of economic instruments, taking into account the approach that the polluter should, in principle, bear the cost of pollution, with due regard to the public interest and without adversely affecting international trade and investment;

Reiterating the commitment to the goals of the Johannesburg Declaration on Sustainable Development and the Plan of Implementation adopted at the World Summit on Sustainable Development in Johannesburg, South Africa, September 2002;

Committed to the Challenges (Principles 15 and 16) and statements on Chemicals (Principles 54 and 55) of the Declaration from the Fifth Ministerial Conference «Environment for Europe», 21-23 May 2003 in, that apply to the problems of obsolete pesticides;

Taking note of ongoing international developments with regard to the design and implementation of Programmes for the stepwise elimination of stocks of obsolete pesticides (with the African Stockpile Programme as an important reference) and the prevention of the build-up of new stocks;

Recognising ongoing national activities and that a large number of Central Eastern and EECCA Countries have expressed their strong concern about the problem and stress the need for a joint approach;

Recognising the expression of broad European and international willingness, as stated in official support letters from 21 Western and Central European and EECCA Countries, as well as from 8 international organisations and a further appeal of 4 former European Ministers of Environment to all European Ministers of Environment in Europe, that concrete steps for a East-West partnership for a Programme of Actions on the elimination of obsolete pesticides in Central European and EECCA Countries have to be made urgently (see Annex 2);

Recognising the supportive letters from EU Commissioner and EU Director General Environment, expressing strong concern on the issue of obsolete pesticides and the recommendation to use available EU Funds such as Cohesion Funds (for the new EU member countries), ISPA and TACIS;

Call on all stakeholders, public or private, to assist Central European and EECCA Countries to eliminate stocks of unwanted hazardous wastes and obsolete pesticides and to establish effective measures to prevent the build-up of new stocks, including pesticide use reduction programme and implementation of Integrated Pest Management;

Undertake to actively support all efforts, applying the principle of common but differentiated responsibilities, to implement national or regional solutions to prevent accumulation of unwanted stocks of hazardous wastes, in particular of obsolete pesticides, and to manage and dispose of existing stocks of such wastes in an environmentally sound and cost effective way;

Recognise that, in order to enable Governments of Central European and EECCA Countries to put into place effective measures to prevent accumulation (including illegal imports) of stocks of hazardous wastes and obsolete pesticides and ensure their environmentally sound management, comprehensive national and regional plans need to be developed and implemented for which financial support should be guaranteed;

Further recognise that the United Nations system, also through the GEF mechanism, is uniquely positioned to provide the appropriate framework for implementing solutions and ensure the concrete and active involvement of other stakeholders, such as industry; and invite UNEP, UNDP, SBC, World Bank, FAO, UNIDO, WHO and EBRD to facilitate the development, implementation and monitoring of a Programme of Action;

Call on all countries of the region to ratify the Stockholm, Rotterdam and Basel Convention;

Recommend that, consistent with the already strongly expressed broad European and international support, donors, including the EU Commission and the GEF, should be encouraged in their funding priorities and budgets, enabling support for the start up and later implementation of a Programme of Action on the elimination of obsolete pesticides in Central European and EECCA Countries;

Recommend that a Working Group be established to develop a Programme of Action, to enable concerted actions in collaboration with governments, appropriate international organisations, international and regional development banks, and other stakeholders, including professional and public interest organisations and industry.

This Programme of Action should include, among others:

- Information on and reference to ongoing activities (such as GEF Enabling Activities, studies related to the EU-Acquis, FAO, UNEP and ACAP), to ensure optimal use of funds and resources and avoid duplication;
- Harmonised methodology for inventories and monitoring;
- Approach for priority setting and assessment of cost effectiveness;
- Ongoing review of existing and emerging technologies for POPs/obsolete pesticides destruction within the framework of existing and future waste management plans;
- Recommendations for the establishment of organisational infrastructure;
- Proposals for the appropriate use of financial mechanisms, such as existing EU and GEF funds;
- Assistance in establishment and implementation of coordination and communication structures;
- Specific programmes for public education and awareness raising, including measures to secure civil society support.

This Programme of Action should serve as a catalyst for the establishment and implementation of Programmes by the Governments of the Central European and EECCA Countries;

Recommend further that this working group should start its multilateral activities without delay using the International HCH and Pesticides Association (IHPA) as an interim platform;

Requesting the relevant international and governmental organisations, as the European Commission, relevant international organisations and bodies including UNEP, UNDP, SBC, World Bank, FAO, UNIDO, WHO and EBRD to sponsor this initiative;

Urge all stakeholders to cooperate on the basis of partnership and to provide advisory services, technical assistance and initial catalytic financial support for a prompt and effective initiation of the work of the working group;

Call on all Governments from the Western and Central European and EECCA Countries to ensure that the draft Programme of Action be put on the agenda of the forthcoming regional/subregional Ministerial Meetings.

The participants express their appreciation for the excellent organisation, facilities and hospitality, provided by the Government and Parliament of Ukraine.

Annexes:

- 1 List of major organisations/participants
- 2 Overview Support Declarations

Annex 1:

List of major organisations/participants of the 7th International HCH and Pesticides Forum, 5 –7 of June 2003 at the National Agricultural University and at the Ukrainian Parliament in Kyiv

International organisations, agencies and NGOs;

AFIDE, AUDACE, BCRCs in Bratislava and Moscow, Crop Life, ECPA, FAO, GEF, IHPA, Nordic Environmental Finance Corporation, OSCE, PAN-UK, Secretariat of the Basel Convention, Syngenta Foundation, UNEP Chemicals, UNEP-IETC, UNIDO

National organisations and NGOs;

ADEME (France), Armenian Ministry of Nature Protection, Armon, Arnika Association, AWHHE, Bakonyalja, Bulgarian Ministry of Environment and Water, DANCEE, Dutch Ministry of Housing, Spatial Planning and the Environment, Sustainable Development and Ecological Research Center Georgian Ministry of Environment, Federal Environment Agency of Germany, German Technical Cooperation, Hungarian Ministry of Agriculture, IPELSKA, Latvian Ministry of Environment, Moldovian Ministry of Ecology, Construction and Territorial Development, Moldovian Ministry of Agriculture, New South Wales Environmental Protection Agency (Australia), Russian Ministry of Agriculture, Russian Ministry of Natural Resources, Polish Ministry of Agriculture, Slovenian Ministry of Health, Swiss Agency for Development Cooperation, Committee on Ecological Policy, Nature Resources Utilisation and Elimination of the Consequences of Chernobyl Catastrophe, Parliament of Ukraine, Cabinet of Ministers of Ukraine, Ministry of Ecology and Natural Resources of Ukraine, Ministry of Agricultural Policy of Ukraine, USAID, USEPA.

Other participants;

United Nations Mission Interim Kosovo, Ministry of Environment and Spatial Planning and representatives of research institutes and the private sector from the mentioned countries and from Brazil, China and Pakistan.

Annex 2: Overview of Support Declarations

Ukraine:

Declaration Ukrainian Parliament
Cabinet of Ministers
Ministry of Agricultural Policy
Ministry of Environment and Natural Resources

International Organisations:

European Commission
European Parliament
FAO
GEF
ECPA/Crop Life
Syngenta Foundation for Sustainable Agriculture
UNIDO
WHO

National Governments:

Minister of Environment, Albania
Minister of Nature Protection, Armenia
Minister of Natural Resources and Environmental Protection, Belarus
Minister of Consumer Interests, Health and Environment, Belgium
Minister of Environment and Water, Bulgaria
Minister of Environmental Protection and Physical Planning, Croatia
Minister of Environment, Czech Republic
Minister for the Environment, Denmark
Minister of Environmental Protection and Reactor Safety, Germany
Swiss Agency for the Environment, Landscape and Forests
Minister for Environment and Agri-Environment, United Kingdom
Minister of Environment, Georgia
Minister of the Environment, Kyrgyzstan
Minister of the Environment, Latvia
Minister of Ecology, Construction and Territorial Development, Moldova
Minister of Foreign Economic Relations, Mordovia, Russian Federation
Royal Ministry of Environment, Norway
Secretary of State, Ministry of Agriculture and Rural Development, Poland
Ministry of Waters and Environmental Protection, Romania
Ministry of Agriculture, Russian Federation
Minister of Environment, Slovakia
Letter of four former Ministers of Environment addressing to the 5th Ministerial Conference «Environment for Europe» the need for official support for the establishment of an Obsolete Pesticides Stockpile Programme for Central European and EECCA Countries.

PRESENTATIONS

**7th INTERNATIONAL
HCH AND PESTICIDES FORUM
KYIV, 5-7 JUNE 2003**

INTERNATIONAL HCH AND PESTICIDES FORUM: BACKGROUND AND HISTORY

John Vijgen

*International HCH & Pesticides Association
Elmevej 14, DK-2840 Holte, Denmark*

The start is actually a very strange story starting in The Netherlands in the town of Deventer, where I was working in 1987, as head of the Soil Remediation Department, worked together with the present members of the IHPA Board, as the issue had affected us considerably

Our company was involved in a large number of soil investigations in the Eastern part of the Netherlands, near the towns of Hengelo and Enschede. Here a huge number of agricultural areas were contaminated with HCH, the residues generated from the lindane production.

During the 50ies a relatively small factory has been first producing the so-called technical HCH and later a specific isomer, gamma HCH or lindane. The problem of this process was that for every ton of lindane around 6 tons of waste (HCH residues have been produced, which were stored around the factory hoping to be re-used in the future. Due to the very fast technical progress of pesticides production the residues became a waste product. At night large amounts of residues were illegally transported and dumped at sand and clay pits, often at agricultural areas.

The heaps lying next to a famous canal, created a huge fish catastrophe and the government was urged to pack the pure waste and arranged finally a transport the salt and kali mines in Germany. Various scandals followed during the years.

At the end of the 80-s the number of contaminated sites were so numerous that all such locations had to be gathered into 1 overall project so-called «Heideweg project» which became then a so-called 10 million guilders Plus project centrally financed by the Ministry of Environment and administered jointly with the Province of Overijssel.

In order to eliminate direct threats to the food production at a number of locations, actions were urgently needed. However there was no existing treatment technology which could fulfil the stringent Dutch values for cleaning the soils.

Thus, we designed an emergency plan, based on the construction of a temporary storage site, built upon a former HCH waste dump that we encapsulated for this purpose. At that storage site all excavated contaminated soils could be piled up in specific classes conform the potential possible treatment methods.

In total about 200 000 tons of contaminated soil have been excavated, stored in the first phase, whereas at the same time a large number of initiatives were taken by the government to push the development but especially the improvement of the available soil treatment technologies. After several years of trials the total amount of soil was cleaned-up around 2001 and the storage site was converted into a local festivity site!

At the beginning of the 90-s we started to question ourselves, is it now pure accidentally that 200 000 tons of this material lies in The Netherlands, or is this issue more a part of an international issue and if yes how do the other ones deal with this issue?

In 1991 the Province of Overijssel agreed with us on hosting the **1st Forum** at the Provincial House in Zwolle and thus in November 1992, we made our start.

The objective of the Forum was to discuss and stimulate participants from all over the world in developing solutions on «how to deal with contaminations originated from HCH and other chlorinated pesticides.

This first Forum showed the large extent of the HCH-residual problem in specifically former Eastern Germany and Basque Country, but brought our attention to the Polish issue of unwanted and obsolete pesticides. The Polish argued, that the problems with HCH do exist, but HCH was just one of A HUGE GROUP OF OTHER PERSISTENT PESTICIDES AND WE HAVE OUR COUNTRY COVERED WITH AT LEAST 60.000 TONNES OF SUCH PESTICIDES. In fact that first meeting led the way to the broader focus to the issue of obsolete pesticides and laid the basis for the scope of the present forum and the regional focus on the specific region of Central and Eastern European countries. This fact was also confirmed by the other Central and Eastern European participants. At the same time the Government of Saxony Anhalt in former Germany offered to host the second Forum in Magdeburg, which we held in 1992.

The **2nd Forum** opened more the gate to the information and understanding from the CEEC/NIS countries and gave insight in the enormous inheritance of former Eastern Germany with production at Magdeburg and Bitterfeld and its waste depositions.

The **3rd Forum** was hosted by the Basque Government in 1994 in Bilbao and showed the enormous extent and consequences of the HCH-production at 2 former production plants, which created for many years the number 1 environment problem of Basque Country. A large number of technical concepts, strategies and alternative solutions have been given.

A continuing input from CEEC/NIS countries was given, but also was stated that the problem was a global problem.

The **4th Forum**, hosted by the Polish Plant Protection Institute in 1996, in Poznan, showed the importance and urgency of the problems in Central and Eastern Europe, but also the difficulty to raise the necessary awareness at that time on national and international level.

An increasing number of Central and Eastern European problems came forward.

The **5th Forum** in Bilbao, Basque country, in 1998, represented a milestone on the achievement of the Basque government in their strategy to tackle fully the nationwide HCH problem. For the present problem owners in CEEC/NIS the Basque strategy is an important example, as most of the funding for the complete elimination of HCH has been largely sponsored by the EU Commission via the Cohesion Fund. This Fund now is from January 2004 open for proposals on obsolete pesticides, as recently stated by Ms. Wallström, from the new EU member states. But this was achieved due to strong and persistent efforts of the Basque government and such common strategy should be applied in the near future!

Just after the 5th Forum, we established the International HCH & Pesticides Association, as a network but without any legal status.

The **6th Forum** in March 2001 in Poznan brought an important change, as the participants called for the concretisation of actions in order to really relieve the CEEC region of its problems, additional to the discussion and exchange of views and the progress and experience of the various technical solutions. Here it showed that technicians were feeling powerless and frustrated and that at things had to be brought to the political level in order to come forward. The 6th Forum was also the first forum, where we had no financial base, provided by the host organisation and where we had to collect each Dollar ourselves! Our sponsors know that and I would like to thank them again to give this so necessary support.

The IHPA has taken the signals from Poznan very serious and has discussed the problems with the various members of the European Parliament, who showed unanimous a strong commitment and willingness to support working towards the necessary sustainable solutions. Thus the EU Parliament sent in July 2001, letters to all Accession countries, requesting them to inform the Parliament on their view on the existence of that problem and if yes to report on the situation and on their strategy in how one intends to solve the problem.

In May 2002, when ecological food was contaminated, as it was deposited in a former pesticides storage in former Eastern Germany, the huge dangers became obvious to the German government, but also the EU Parliament and the EU Commission. The dangers of food contaminated by obsolete pesticides from the Accession countries became now a cold reality for the present EU-Member States. Also in July that year members of the Parliament have ques-

tioned again Commissioner Wallström to take steps to tackle this problem.

On November 4th last year in Brussels during a Stakeholders' Conference on the Development of a Thematic Strategy on the Sustainable Use of Pesticides, Ms. Margot Wallström showed strong concern, when we talked to her and she promised to address the issue in her cabinet and do whatever was possible.

Politicians have increased pressure onto the Commission to act now, by their recent letter to the governments of the 10 Accession Countries, which was signed by not less than 28 Members of the EU-Parliament.

In June last year Mr. Terytze, one of our Board Members and I visited Ukraine, in order to find out the options and the interest of the authorities and research institutes to host the **7th Forum** in Ukraine.

Until the last day of our visit we really had our doubts if we would be able to hold the forum here, but on the last day, we had an appointment with two highly engaged ladies, Valentyna Pidlisnyuk and Tatyana Stefanovska which I had met a year before in Germany, for a final drink. We discussed our doubts and worries and as by a kind of miracle they both said, we can do the job and hold your forum at the National Agricultural University! And on the last Saturday we paid a visit to the University check up all facilities and agreed with such highly motivated organisers we must give it a try!

During the preparations, in the following months, our Ukrainian team, headed by Prof. Valentyna Pidlisnyuk, Tatyana Stefanovska, in close co-operation with Alla Kravchenko and others and fully supported by rector Melnychuk, the forum has found increasing backing from the Ukrainian government. We are very glad with the support of The Committee of the Ukrainian Parliament on Ecological Policy, Nature resources utilization and Elimination the consequences of Chernobyl catastrophe has declared on January 23rd its full support and has included the forum in its official Plan of activities. And we have to thank especially Mr. Ivan Zaetz, who has been doing every possible effort to support us. Further we have received unanimously full support of the Cabinet of Ministers of Ukraine, the Ministry of Ecology and Natural Resources of Ukraine and the Ministry of Agricultural Policy of Ukraine. It may be also clear that the problem of obsolete pesticides can simply not be solved without the necessary political support and commitment now and in the future!

Our requests for the support of the idea of a programme /fund of Action to eliminate has culminated in support letters of 20 European Governments, 8 international organisations and an urgent letter to all ministers of Environment by former Ministers Environment of Denmark, Finland, France and The Netherlands. We also have to thank the official participants at the 5th Ministerial Conference, environment for

Europe, which has now for the first time included obsolete pesticides as an important concern in its Declaration.

Also the initiative of The Committee of the Ukrainian Parliament on Ecological Policy, Nature Resources Utilization and Elimination the Consequences of Chernobyl Catastrophe to host a discussion at the Ukrainian Parliament on May 22nd under participation of EU Parliament members has shown the enormous commitment to really act and not restrict to only talk!

We hope that you all will support an important declaration for adequate and urgent actions. We will try to distribute a draft declaration this morning and hope that most of the remarks and input will be included during the day and tomorrow morning, so that we will have a common declaration which will show the way forward for all of us!

Specially, I like to thank the hosting organizations:

National Agricultural University, Ukraine

Federal Environmental Agency, Germany

Sustainable Development and Ecological Research Center, Ukraine

International HCH & Pesticides Association, Denmark

And the co-operating organisations:

Committee on Ecological Policy, Nature Resources Utilization and Elimination of the Consequences of Chernobyl Catastrophe, Parliament of Ukraine

Cabinet of Ministers of Ukraine

Ministry of Ecology and Natural Resources of Ukraine

Ministry of Agricultural Policy of Ukraine

I like to thank the sponsors, as mentioned before by Ms. Pidlisnyuk:

Without their financial support this event would simply not have been taken place and we encourage you to help us

again in the future, as we need your continuous support!

On the program I like to spend some final words:

Apart from the common sessions, which has a special highlight with the Destruction Technologies, where normally hot debates take place I like to mention some new issues:

On special request of the Ukraine, we have included a large monitoring session running over 2 days, which expresses the large experiences available in Ukraine on this field.

Also the Poster session is grown considerably and has been split up in 3 sections in order to give more attention to each special issue.

New is the Workshop on Phytoremediation, giving a new dimension to pesticides soil pollution, as recently been shown in the African Stockpile Program, where large amounts of soil have now come across. The areas around the stocks are often quite large, but also large agricultural areas are known. In Ukraine, around 15-20% of the agricultural soils is polluted with DDT and 5% with HCH. Large areas have been polluted in Uzbekistan. How can one clean such huge areas? Taking these amounts on a shovel and put them into a treatment plant seems fantasy, but in situ treatment by means of plants, could be a new alternative for problem owners, such as farmers, with small budgets, but the need of clean soil.

On the 3rd day we can offer an interesting trip to obsolete pesticides stocks and at the same time, a phytoremediation training for trainers, will be held by top phytoremediation specialists Steve Rock, Peter Kulakow and Barbara Zeeb. This training has the objective that Ukrainian specialists will teach thereafter problem owners/farmers solutions in order to bring down heavy loads of pesticides in their soils to lower levels in the future.

I wish you all a good exchange, making of many new friendships and co-operations and a good working towards real elimination of the obsolete problem in the region.

OBSOLETE PESTICIDES: HISTORICAL DISASTER OR RECURRING NIGHTMARE?

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BACKGROUND

The consequences of past errors in pesticide supply and management are well known and well documented. These include accumulations of an estimated half a million tones of obsolete pesticides and directly associated contaminated soils and other materials in Africa, Asia, the Near East, Latin America and the region of Easter Europe, Caucasus and Central Asia (EECCA). In addition pesticide containers have corroded or been physically damaged in ways that have allowed their contents to disperse causing serious environmental contamination and risks to human and animal health.

The risks to health and environment are high, since the chemicals that are found in obsolete pesticide stockpiles are typically of the more persistent and toxic groups such as organochlorine, organophosphate and carbamate insecticides, dithiocarbamate fungicides and phenoxy acetic acid herbicides. Leakage of pesticides has resulted in dispersal of the chemicals in air, water and soil and exposure of people and the environment through direct exposure and indirectly through consumption of contaminated water and food. The acute toxic effects of exposure are sometimes reported and recorded, but the chronic effects have never been researched.

The Potential solutions to these problems are well known and include effective quantification of the stocks by carrying out detailed inventories. The waste must then be repackaged by appropriately trained and equipped expert teams, and finally transported for treatment or destruction in facilities that meet the highest regulatory requirements.

There are many barriers to implementation of these solutions effectively, and these are also known. The major barrier is lack of finance, others include lack of technical capacity in the countries affected by obsolete pesticide stockpiles, resistance among both national governments in affected countries and donors to prioritise obsolete pesticides for action, lack of public awareness, lack of appropriate equipment and materials to deal with problems and weak supporting infrastructures, among others.

The causes of obsolete pesticide accumulation are well documented and include the following factors:

- Over ordering or oversupply
- Uncoordinated donations or purchases

- Poor storage
- Inappropriate formulation or package size
- Product deterioration
- Legal controls introduced after the pesticides were purchased

The efforts to address the problem of obsolete pesticides have been severely limited and as a result of a lack of financial and technical resources have also been inadequate. They include:

- Pesticides were poorly stored
- Unwanted products were buried
- Stocks were forgotten
- In the worse cases stocks entered the marketplace

As a result No country is immune from the problem of obsolete stocks, and yet no country has comprehensive solutions in place to solve and prevent the problem.

During the time the FAO has been gathering inventory data on obsolete pesticides in developing countries the figures have risen dramatically as illustrated by Figure 1 below.

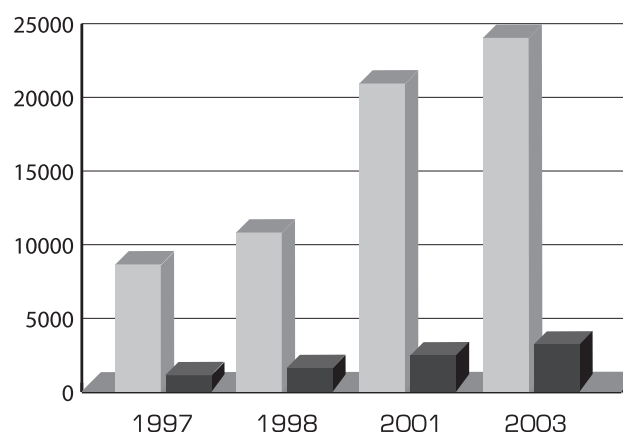


Figure 1: Obsolete pesticide stocks recorded by FAO indicative inventories

Undoubtedly the increases are due in large part to the fact that inventories themselves are getting better. More training has been provided so that those carrying out inventories gather more accurate data and process it more accurately. Internationally data is collated more rapidly and maintained more consistently. FAO for example has an assistant devoting much of her time to updating inventories of obsolete pesticides.

Nevertheless, the question needs to be asked whether any of the causes of obsolete pesticides listed above are still occurring so that existing stocks are not only being documented more accurately, but are actually growing because new products are being added to the stockpiles.

In terms of oversupply it is still true that humanitarian and food security emergencies are still the biggest sources of bulk pesticide donations. These are generally uncoordinated, sometimes unsolicited, often not well specified and commonly arrive into an administrative vacuum. Many major international agencies contribute pesticides in this way, and do not generally have the necessary safeguards in place to ensure that the pesticides will be properly managed and stored, will reach their point of use in good time and be used by appropriately trained and equipped people. The emergency situations during which such pesticides are supplied generally result in rushed decision-making, shortcutting of procedures and are frequently associated with a lack of governance in the recipient countries. These situations inevitable create a higher risk that pesticides will become obsolete and indeed there is clear evidence of this having happened in Ethiopia, Mozambique, Madagascar, Afghanistan and Iraq in recent years.

The strategic pesticide stocks that have contributed to some of the biggest obsolete pesticide stockpiles currently in existence are still maintained in many countries. These are stocks of pesticides that are held for rapid mobilization in case of major pest outbreaks. Proposals have been developed for alternative strategies such as stock rotation, reducing stocks of formulated products and relying on rapid formulation of products when they are needed, use of biological control agents and better monitoring to avoid emergencies. In some countries such strategies have been successfully employed. Nevertheless, some countries still maintain static strategic stocks that pose a high risk of becoming obsolete in the coming years.

Poor storage of pesticides is still rife in most developing countries. Even stores from which obsolete pesticides have been recently removed are commonly found to contain new pesticides that are dispersed around the store, stored in such a way that FIFO stock management cannot be effectively applied, or mishandled such that packaging is damaged and labels are missing. Better and more training is badly needed throughout the developing world and among all those who hold pesticide stocks. Similarly better storage facilities for pesticides are sorely needed so that stocks can be managed better.

Formulated pesticides still have a limited shelf life that is normally about two years. In remote parts of developing regions such as Africa it can take over a year for products to reach their end point of use. In such situations products can be technically obsolete soon after they arrive and cases have been found where the products were already expired on arrival. Such situations can be remedied with better distribution systems and through the provision of products and packages of pesticides that are more appropriate to such remote locations.

The issue of pesticide container management remains unsolved in most countries, even developed countries.

There are very few examples of successful schemes that remove empty pesticide containers from use in developing countries. As a result the ever increasing quantity of metal drums, plastic canisters and jugs and small metal, glass or plastic bottles continue to circulate and retain their value as usable and frequently marketable products. There is an urgent need for industry, government and other stakeholders to develop and implement effective systems for reuse, recycling and safe disposal of empty pesticide containers in developing countries.

Mishandling of pesticides that leads to serious spillage and resulting intoxication and environmental contamination continues to occur. This is probably largely due to a lack of understanding of the hazards associated with pesticides on the part of those handling them. Pesticides and other hazardous chemicals should always be handled in accordance with best practice in health and safety that relates to such materials. They should never be handled by untrained, inexperienced and poorly equipped personnel, yet this is often the case, particularly in developing countries.

What needs to be done?

NO DISPOSAL WITHOUT PREVENTION

Wherever obsolete pesticides are addressed through disposal operations or related activities, equal status must be given to careful design and implementation of prevention measures. These should address the entire life cycle of pesticides in the country concerned and ensure that weaknesses are identified and addressed to ensure that pesticides will be regulated and managed in accordance with best practices in the future.

TECHNICAL SOLUTIONS THAT ARE:

- Viable
- Cost effective

Solutions to pesticide management issues that are proposed to developing countries must be both viable and cost effective in the situations where they will be applied. For example, container recycling programmes must ensure not only that the facilities for handling the materials exist, but that there is a market for their end product and that the value placed on containers is at least as high as their current market value. Similar thinking must be pursued in all aspects of pesticide life cycle management. However, where no viable and cost effective solutions to problems are available then thought must be put into avoiding the problem in the first place. Such examples might include legislating for container re-use or banning the import of highly hazardous pesticides.

TRAINING

More and better training is identified as a need in many of the examples given above. All responsible parties including government, industry, user groups, NGOs, aid organizations and others should engage with the need for development and delivery of effective training on the handling

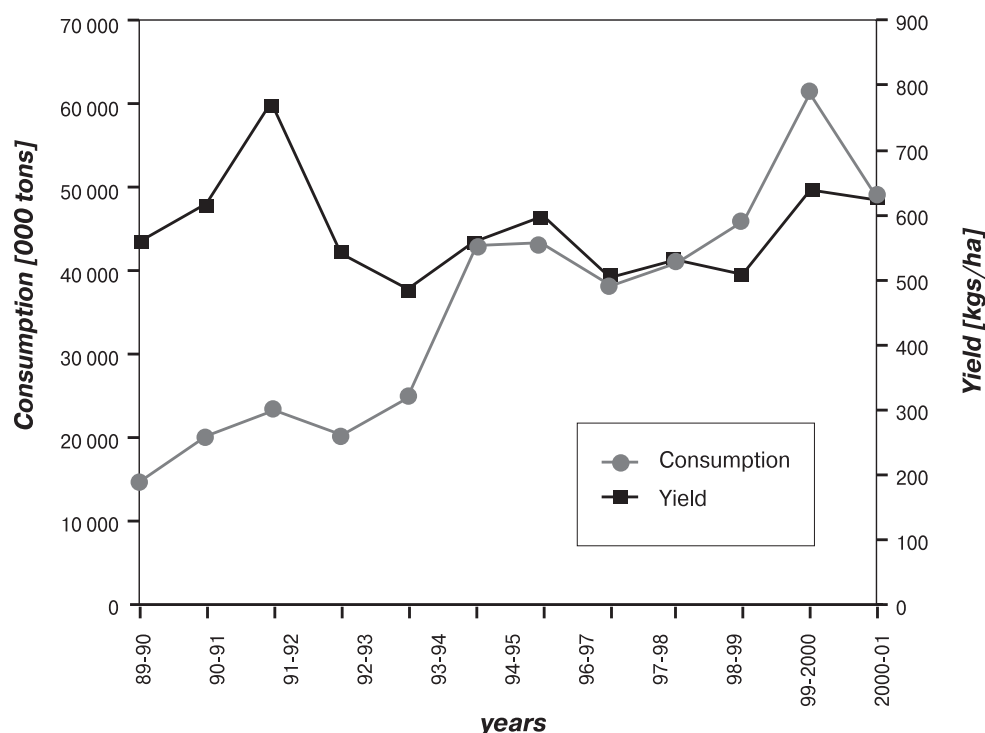


Figure 2:
Pesticide Consumption and
Average Cotton Yield 1990-
2001 in Pakistan.

and use of pesticides. Efforts must also be directed at ensuring that training is delivered to the correct personnel and that it is refreshed regularly.

MONITORING

The effectiveness of regulation, enforcement, training and any management systems that are put in place for the handling and use of pesticides should be independently monitored on an ongoing basis to ensure that the required results are being achieved.

REGULATION

Regulation should be reviewed and updated, modified or supplemented to ensure that the appropriate bodies are empowered to act against problems that arise with the life cycle of pesticides. Regulations should also be designed to give clear unambiguous information on the expectations from all those involved in the life cycle of pesticides. Regulations should also be enforceable and should allow the stakeholders concerned to continue to fulfill their functions.

ENFORCEMENT

Regulations must be enforceable and the infrastructure and resources for their enforcement should be made available. Too commonly countries develop legislation which cannot be enforced because there is no budget for staff or vehicles to carry out the necessary tasks.

MOST IMPORTANTLY, AVOID USING PESTICIDES

Reducing reliance on pesticides is undoubtedly the most effective way of preventing the accumulation of obsolete pesticide stockpiles and many of the other problems associated with pesticide use.

In technical terms it is possible to reduce the impacts of pesticides by applying reduced volumes by means of low volume application techniques; using low doses that can still effectively control pests but are lower than recommended doses; using less hazardous formulations and in particular avoiding WHO Class 1 products, and avoiding low quality low cost products that may be contaminated or less effective than more costly products.

The wider support and promotion of crop production and pest management techniques that eliminate or reduce reliance on pesticides can demonstrably help poor farmers to generate larger incomes. Their expenditure on external inputs is reduced, yields are the same or can be higher than crops grown with external inputs, and hence end of season margins are larger, as illustrated in figure 2.

Clearly if farmers use fewer pesticides, distributors will import less and hence the ultimate risk of obsolescence and stockpiling will be reduced. This is only one of many benefits associated with reduced reliance on pesticides.

AND FINALLY:

If we are truly serious about solving the problems of obsolete pesticides and hence making ourselves redundant, we must:

- Take note of the causes of obsolete pesticides
- Make prevention a priority
- Develop effective solutions
- Avoid the root causes of the problem by reducing reliance on pesticides

COMPREHENSIVE INVENTORY AND IDENTIFICATION OF OBSOLETE PESTICIDES AS A PRIOR DIRECTION FOR ANSWERING POPs PROBLEM IN UKRAINE

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Obsolete pesticides (OP) represent a special group of highly toxic substances that can no longer be used as a result of their expiration, prohibition, labelling loss or uncontrolled mixing.

OP stockpiling started as early as the 1970s after prohibition of many pesticides. At that time, the Council of Ministers of the USSR issued an executive order prescribing collection of OP at the regional sites with following transportation to the sites of their manufacture (mostly in Russia) for treatment or disposal. Due to economical considerations, the manufacturers were not interested in taking the OP from regional sites, so none of the collected chemicals were transported back to plants for treatment.

Mostly, OP were collected at storage facilities that were unsuitable for long-term storage of hazardous chemicals. The stockpiling process ran in a practically uncontrolled way.

In what followed, the owners of the OP stores have changed a few times. This resulted in loss of labelling and documentation, in wrecking of storage facilities and as well as packing materials and containers, and in formation of assorted mixtures of unknown origin. Moreover, many facilities do not have any legitimate owners at all. Thus, a great possibility of illegal access to such facilities and therefore illegal use of the stockpiled OP exists.

For the most part, both the present state of storage facilities and the storage conditions are inadequate. There are strong grounds for believing that during the long period of storage many chemical reactions have occurred that resulted in the formation of new hazardous substances. This makes the chemical identification and further management more difficult and significantly increases the overall hazard associated with these OP.

The major risks associated with stockpiled OP are as follows:

- Adverse health and environmental effects;
- Possibility of illegal access and use of OP.

Therefore, developing methods for safe OP management in order to dispose them is of great importance.

The main direction in solving the OP problem should be a comprehensive inventory of stockpiled OP and storage facilities, degree of hazard posed by the facilities, and investigation of ownership. Only after such inventory has

taken place it will be possible to classify the storage facilities according to their degree of hazard and to set plans for appropriate actions.

In accordance with a joint executive order issued by the Ministries of Agricultural Policy, Ecology and Natural Resources, and Public Health, in 2001-2002 a comprehensive inventory of stockpiled OP was performed. Its execution was assigned to local state administrations and the above-mentioned Ministries' divisions. Methodical matters were worked out by the IEC. The IEC has also trained members of inventory commissions.

The 2002 inventory data have shown that there is not less than 15,500 tons of OP stockpiled in Ukraine, including 8,500 tons located at the so-called «central stores». There are 147 stores of this kind. Furthermore, around 7,000 tons of OP is stored at 4,976 scattered storage sites owned by different judicial persons.

More than 20 % of OP is placed in the open air and 30 % of stores are almost ruined. Actually each Ukrainian region has its own storage sites.

OP is divided into three categories: banned (A category), expired (B category) and mixed and unidentified (C category). The overall amounts of OP are divided among these categories as follows: A, about 30 %; B, about 20 % and C, about 50 %. Approximately 40 – 50 % belong to chlororganic substances.

Regretfully, in many instances these inventories have been carried out as a desk study based only on existing records. A sample survey of storage sites was performed by the IEC, including OP repacking and weighing, has shown that the data collected during the desk studies sometimes did not take into account the actual mounts of those OP which were spilled and mixed with foreign matters, such as construction wastes. There are reasons to assume that the actual amounts of other OP categories are not always in line with the inventory data.

According to our own conservative estimates, the actual stockpiled OP amount in Ukraine exceeds the official data by 1.5 times. Such discrepancy complicates OP management planning and the necessary costs estimation.

Under the Danish-Ukrainian project «Elimination of Risks Related to Stockpiled obsolete Pesticides in Ukraine», a set of guidelines on conducting comprehensive inventory have been worked out. Taking into account that OP are placed at many sites scattered all over the country with each site having its own distinctions, the general approach should include identification of the greatest risks and finding the cheapest ways for their minimization.

A set of guidelines on conducting comprehensive inventory was worked out. The IEC has also trained members of inventory commissions for several regions.

Our approach consists of four steps:

- Step 1 – Survey,
- Step 2 – Risk assessment,
- Step 3 – Deciding ways for risk elimination,
- Step 4 – Prioritising measures to minimize the risks.

The need for chemical identification of stockpiled OP is determined on side. Our experience shows that simple ele-

mental analysis is sufficient.

Inventory can consist of three stages.

Stage 1 Includes technical training and safety instructions for working with OP.

Stage 2 Includes survey and inventory and consists of the following steps:

- Survey planning,
- Survey performance, samples collection,
- Reporting of the obtained results.

This stage also includes elaborating recommendations on further site management.

In Stage 3 measures for eliminating danger posed by the storage sites are taken (i.e., repacking, sorting, segregation).

In order to solve the stockpiled OP problem in Ukraine, the following steps should be taken:

- Establishing a state task force with regional departments for handling all the tasks concerning stockpiled OP;
- Comprehensive inventory of storage sites, including repacking and weighing of OP;
- Chemical analysis of OP in order to determine heavy metals content (particularly arsenic);
- Establishing in each region a proper facility for rendering OP harmless and/or their destruction.

ELIMINATION OF RISKS RELATED TO STOCKPILED OBSOLETE PESTICIDES IN UKRAINE

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ing account of the Country's present economical conditions.

FIGURE 2:

Future main storage in Lozovaya Ukraine before re-building 2003

To promote this development, with donor support from the Danish Cooperation for Environment in Eastern Europe, a National Plan for Elimination of Stockpiled



Figure 1



Figure 2



Figure 3

The current situation in the field of hazardous waste, here-under obsolete pesticides (OP), management in Ukraine can be characterised as critical. Up to 22,000 tons or even more of 1st and 2nd hazard class is assumed stockpiled throughout the country, and frequently stored under unsuitable or alarming conditions posing the environment and human health at extreme risk. The situation is aggravated by the lack of efficient regulatory instruments as well as appropriate technical and institutional infrastructure.

FIGURE 1:

Existing pesticide storage in Lozovaya - Ukraine 2003

This situation envisages establishing of appropriate legal basis, development of long-term national programme, establishing of an efficient managerial structure, and introduction of new technological solutions tak-

Obsolete Pesticides has been developed for the Ministry of Environment and Natural Resources and for the approval by the Verkhovna Rada. As obsolete pesticides are classified as toxic waste, the Plan is subjected to the National Programme for Toxic Waste Management.

FIGURE 3:

Storage in steel containers, before repacking, Lozovaya, Ukraine 2003

In the Phase I of the project three pilot projects were prepared in co-operation with the appropriate administrations and owners of the involved facilities. These were: «Interim storage facility in Lozovaya District, Kherson Oblast», «Cement kiln incineration at Kherson cement plant» and «Mobile incinerator, based on a reconstructed military rocket fuel after-burner».

FIGURE 4:**Emptying and repacking obsolete pesticides from a steel container in Poltavskaya, Lozovaya, Ukraine 2003**

The Danish Government decided in the spring 2001 that they would not support incineration of obsolete pesticides (and any other kind of hazardous waste) in cement kilns. In addition it turned out to be rather expensive to use local Ukrainian mobile incinerators in the treatment of the obsolete pesticides and this part of the pilot projects has also been stopped. The third pilot project, the reconstruction of a pesticide storage in Lozovaya is however alive, and is ongoing. In connection with these pilot projects 5 different management training projects is also planned:

FIGURE 5:**Use of GIS has been used as database for the registration of the new inventories based on the packed obsolete pesticides**

-Training in Pesticide Management in NCHWM and MER

-Training in business plans development in NCHWM and MER

-Introduction to GIS to be used as database in connection with pesticide inventory in NCHWM, IEC and -MER. Also creation of a proper homepage is part of this project.

-Training in PR- management

-English course for more than 30 persons in Kiev and Kharkiv

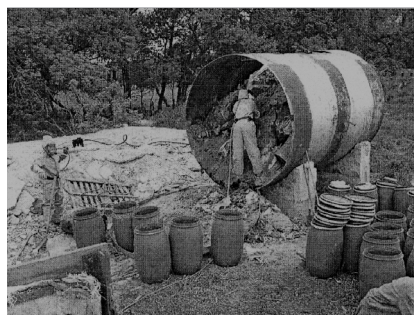
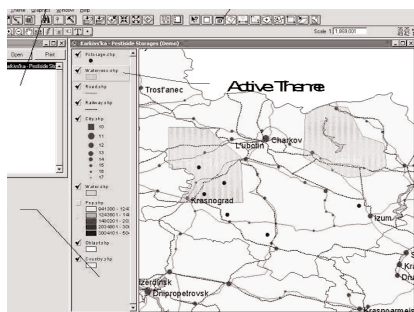
FIGURE 6:**Cleaned steel tank in Poltavskaya, Ukraine 2003**

A part of the project is also to spread the methodology developed in Lozovaya, to cover all 27 Oblasts in Ukraine. The idea is that the Danish specialist and the Ukrainian specialist, travel from Oblast to Oblast, and train a collection and clean-up team in every Oblast. The travelling specialists shall be assisted from the central Kiev NCHWM/MER-office by the group trained in «Pesticide Management». Furthermore a seminar for two people from each Oblast is planned in Kiev. These two people shall also assist the travelling specialists.

FIGURE 7:**Samples are taking of each batch, ready for later analyses, Ukraine 2003**

Figure 8: Packed obsolete pesticides in main storage in Lozovaya, Ukraine 2003

Finally the clean-up teams will create a full description of the inventory, which they will file in a computer according to international standards, and send to Kiev to be registered by the group trained in GIS.

*Figure 4**Figure 5**Figure 6**Figure 7**Figure 8*

INVENTORIES OF OBSOLETE PESTICIDE STOCKS IN CENTRAL AND EASTERN EUROPE

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BACKGROUND

Stocks of obsolete pesticides are widespread in the world. They form a severe threat to human health and can cause irreversible damage to the environment.

Addressing this problem of obsolete pesticides requires:

- Awareness of the problem on the political and public level.
- Adequate political will, as well as technical and financial capacities.
- A step-wise approach, starting with detailed, nationwide inventories followed by systematic, prioritised disposal programmes.

The situation in Central and Eastern Europe (CEE) is a special one. Following the transition to a market economy, many of the existing state farms and village co-operatives in the countries of CEE have ceased to function and are subject to privatisation processes. One of the consequences of these developments is that stocks of pesticides and other chemicals are often left under poor management and control.

The threat of these stocks of obsolete pesticides is recognised in most CEE countries and in the years following 1990 a number of bilateral and multilateral activities have been initiated to address this issue. However, a structured, coordinated and cost-effective approach to address the problem has not yet been developed. The main reasons for this are that 1) the actual size of the problem is often unknown, 2) lack of technical capacity, and 3) lack of finances.

The 6th International HCH and Pesticides Forum held in Poznan, Poland, in March 2001, also addressed the problem. The recommendations of that Forum called for:

- Production of nation-wide inventories of obsolete pesticides in the countries of CEE as a matter of priority;
- The establishment of mechanisms for regional collaboration, including a regional advisory body, regional resource centres, a regional CEE website and a regional database of stocks of obsolete pesticides;
- Support from outside the CEE region.

FOLLOW-UP IN SLOVAKIA AND HUNGARY

As a follow-up of the Poznan Forum, the Slovak-Hungarian environmental NGO "Ipel'ska unia" (Ipel' Union) was planning to conduct nation-wide inventories of

obsolete pesticide stocks in Slovakia and Hungary in the period of 2002-2005.

In order to build practical experience in locating stocks of obsolete pesticides and in order not to lose the momentum, the Ipel' Union intended to carry out a pilot inventory in the Ipel' watershed region in Slovakia and in one or two regions in Hungary.

For this the Ipel' Union requested the Dutch Ministry of the Environment for technical support in developing and carrying out these pilot inventories.

In response to this request, and in response to recommendations of the 6th HCH Forum, the Dutch Ministry of the Environment initiated a 12-month project with the following objectives:

1. Providing technical support to the Ipel' Union in developing and implementing the pilot inventories in Slovakia and Hungary;
2. Assisting the establishment of mechanisms for regional collaboration including:
 - producing a practical manual for (pilot) inventories for CEE countries,
 - developing a regional CEE website for obsolete chemicals and preparing a regional database of stocks of obsolete pesticides.

The project resulted in:

1. A completed **pilot survey** in Slovakia for which the followed strategy is characterised by:
 - Collaboration between NGOs, national and local governments, academia and involved institutes and organisations. Top-down information from the national Government (amounting to nine storages in the pilot region) is combined with bottom-up information from mayors, local agricultural organisations and NGOs (amounting to 63 storages reportedly containing obsolete pesticides in the pilot region).
 - Health and safety considerations. The fieldworkers, who gathered the 'bottom-up' information by visiting villages, were trained in health and safety issues concerning obsolete pesticides and were not to enter the storages.
 - Public information campaign. A target group of mayors (229), agricultural enterprises, (140, mostly former cooperative farms), and forestry companies (6) in the pilot region were informed of the project in a self-reporting campaign.
 - Prioritisation of the located storages with a view to the allocation of limited resources. Next to information about the locations, the fieldworkers gather information about the storage conditions and other variables related to the estimated threat each storage poses for the environment and human health, such as distances to vulnerable object such as streams, vegetable gardens, et cetera.

In Hungary a similar pilot survey project is being conducted in the period 1 September 2002 - 1 September 2003, also based on the cooperation of all stakeholders and with a combination of a "top-down" and "bottom-up" approach.

2. A secured **web-based database** for documenting the collected data about the location of the storages of obsolete pesticides and the conditions of storage. The database functions to enable:

- efficient prioritisation of storages,
- efficient execution of inventories (i.e. expert analyses)

of the located storages, efficient production of progress reports.

3. A CEE regional **Obsolete Chemicals Website**. The website features the possibility (for possible future CEE national coordinators) to remotely update specific web pages for which special authorisation can be given. In this way regional cooperation and dissemination of experiences can be more easily realised.

A practical survey manual for the preparation and implementation of surveys of stocks of obsolete pesticides, using the methodology and infrastructure produced in the Slovakian and Hungarian pilot surveys.

ORGANISATION OF THE PROJECT

Financial resources were made available through the Dutch - Slovakian Partnership in the Field of the Environment that provided 30,000 EUR for surveys in one province of Slovakia. The Dutch - Hungarian Partnership for Accession supported the survey in three regions of Hungary and the design and management of a CEE obsolete chemicals website and database with 50,000 EUR.

The Slovak-Hungarian NGO Ipel' Union was responsible for the project coordination in both countries, working in close cooperation with the REFLEX Environmental Association in Hungary. A Supervisory Board was established from the representatives of the Ministries of the Environment and Agriculture of Slovakia and Hungary. The Dutch Ministry of the Environment set up a Guidance Committee of experts to provide assistance for the project team.

Survey materials, including training manual and storage forms, were developed conform to FAO standards. To enable efficient inventories, prioritisation and progress reports, a CEE obsolete chemicals website and a web-based, password-protected database analogue to storage form was designed (www.obsoletechemicals-cee.org/chembase).

As part of the information campaign an informative letter presenting the goals of the project and a self-report form was sent to every municipality, agricultural farm and NGO in the survey area. The campaign resulted in a response rate of 10% in Slovakia and 61% in Hungary of forms sent back to Ipel' Union. Information about the project was given to local, regional and national media as well.

A training course was organised for the field workers. In Slovakia 20 student field workers were trained in a 3-day course. The participants were provided with background information about the project, the use of pesticides in agriculture, the extent of the problem of obsolete pesticides with a special focus on the situation in CEE, the survey method that was applied in the project, health and safety issues, development of basic communication and social skills and filling in the inventory forms and working with the manual. Field trips to three selected agricultural farms were included.

In Hungary a two-day training was held in September 2002 with the participation of five experienced NGO field workers.

Two approaches in collecting data were combined to maximise the results of the surveys:

- Collecting data of obsolete pesticides from central and regional administrations, archives and officials (a 'top-down approach'), and

- Visiting villages, contacting mayors, interviewing local officials, inhabitants and NGOs and visiting agricultural organisations (a 'bottom-up approach').

RESULTS

The objective of the pilot surveys was to obtain a detailed list of locations or potential locations of stocks of obsolete pesticides in the Ipel' watershed region in Slovakia, and the central Trans-Danubian area in Hungary. The survey activities in the 229 Slovakian municipalities resulted in 63 locations reportedly containing stocks of obsolete pesticides. The Governmental archives listed nine storages in the region. The estimated quantity of pesticides in the total of stocks was over 50 tons. The storage conditions were in many cases not sufficient.

In contrast to the Slovakian "quick-sweep" approach, the survey of 410 municipalities in Hungary started in September 2002 and finished at the end of May 2003. Analyses of the gathered data are still in process. Up to 15 May 2003, 42 storages of obsolete chemicals were localised in 158 municipalities. The Governmental information in the case of Hungary was unserviceable to the project because the data did not differentiate between obsolete and usable pesticide stocks. The overall quantity of the found pesticides in the Hungarian pilot region is estimated at 46 tons, plus 330 m³ of empty packaging material. Conditions of storage in 14 stocks were not sufficient.

DEMONSTRATION CLEAN-UPS IN SLOVAKIA AND HUNGARY

Experience with a small scale project carried out in 1997 in collaboration between the Bakonyalja Association, a small Hungarian NGO, and the Netherlands Ministry of the Environment, showed that a demonstration clean-up can not only enhance public awareness of the problem of obsolete pesticides, but also help to convince those who are responsible for obsolete pesticide stocks to provide information for the surveys. Therefore, with the financial assistance of the UK Department for Environment, Food and Rural Affairs (DEFRA), a small number of demonstration clean-ups were carried out to facilitate ongoing survey activities.

The demonstration clean-ups in Hungary were coordinated by the Ipel' Union and Reflex Association, and a total of five clean-ups were implemented, one prior to the survey and four during the survey. The storages were selected on the basis of the potential danger they posed on the environment and human health. The 16 tons of obsolete pesticides and packaging material were incinerated in Győr, Hungary.

The situation in Slovakia is more difficult, since no adequate disposal technology complying with EU legislation exists in the country. For this reason the Dutch guidance

committee advised on exporting the chemicals to Hungarian incinerators that comply with EU standards by way of a demonstration clean up. Also, on a more structural level, the guidance committee concluded that the treatment of hazardous wastes should be viewed on a regional level, for which the demonstration export could be catalytic.

CONCLUSIONS AND FOLLOW-UP

Experiences during the survey in both countries showed that mayors, NGOs and local people are collaborative, but in many cases cannot provide information about the locations of obsolete pesticide storages. In many cases the public is unfamiliar with obsolete pesticides and their related threats to human health and the environment. Mayors are good sources of further contact information.

Employees and former employees of agricultural farms often have information concerning storages, but can be found anxious to participate with a view to possible sanctions.

Issues that need to be considered for future surveys include provision of better information for target groups

about the nature of obsolete pesticides and the problem in general. This could be done by publishing information flyers and distributing them to potential interviewees prior to survey activities. On the basis of the pilots, a more intense media campaign, including demonstration clean-up activities is expected to result in a more cooperative stance of interviewees. Also, updated contact information of target groups would benefit the results of future projects.

The results of the pilot surveys have been used as a basis for proposals to obtain funds for detailed nationwide surveys and expert inventories of obsolete pesticide stocks in Slovakia and Hungary. Some proposals are under evaluation, but others, classified as eligible for application and amply meeting the standards for submission, have not been granted. A CEE-wide regional coordinated Program of Action that includes mechanisms for prioritisation and cost-effectiveness therefore needs to be complemented with support from national Governments, donor agents and environmental programs within and outside the region.

PCDDs/FS CONTAMINATION OF THE SURROUNDINGS OF SPOLANA NERATOVICE BEFORE AND AFTER FLOODS 2002

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INTRODUCTION

The Spolana Neratovice factory is at this time probably the most known source of POPs contamination in the Czech Republic. The chemical factory of Spolana Neratovice is situated approximately 25 km north of Prague at the Elbe River. It produced in the period of 1965-68 the chlorine herbicide 2,4,5-T and chlorinated phenols. A part

of 2,4,5-T was even exported to the USA and was applied as a component of "Agent Orange" in the Vietnam war. Due to breaking technological conditions during the production, a huge amount of dioxins (in particular, the most toxic 2,3,7,8-TCDD) was formed, and former factory buildings containing products, intermediates, installations, etc. currently belong to the most dioxin-contaminated sites on the globe. Moreover, soil in the factory is highly contaminated with organochlorine pesticides that were produced there. The 2,4,5-T and chlorophenols production was stopped in 1968 when about 80 cases of occupational diseases developed (55 workers were hospitalized mainly with severe chloracne manifestations and porphyria). (Pazderova-Vejlupkova et al., 1981, Pelclova et al., 2001).

The production was stopped in 1968 and former production buildings were closed, but unfortunately they were not decontaminated or destroyed up to date. This site is still a big potential source of contamination of the Elbe river by OCPs and PCDDs/Fs.

Chemical analysis proved an extremely high degree of contamination of waste products stored in production buildings, building walls and floors, air, soil and groundwater. The highest concentration of dioxins (over 24 ppm of 2378-TCDD) was measured in the residues of chemical substances. It is assumed that there are tonnes of this waste stored in the buildings.

The Spolana factory, including some of the dioxin-contaminated buildings, was flooded in 2002 and one can expect dioxin release into agricultural fields and the Elbe River as well as in its sediment. An extent of environmental contamination was given, as well as to start with the

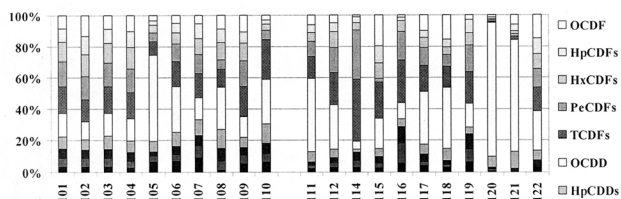


Figure 1: The comparison of 2,3,7,8-substituted congeners of PCDDs/Fs from reference soil samples collected in the Czech Republic before and after floods 2002 and from the samples collected in the surrounding of Spolana Neratovice

definitive solution of dioxin-contaminated buildings and soil in their vicinity in Spolana Neratovice. (Zemek and Kocan, 1991, Kocan et al., 1991).

MATERIALS AND METHODS

More than 100 samples (21 soils, 33 sediment, 27 waters, 2 wastes, 21 biotic and food samples) were analyzed for the PCDDs/Fs contents before and after floods from the company surroundings. Additionally, 14 samples of sediments from other sampling sites of the Elbe basin were collected and analysed. In total, 118 samples were analysed (19 before and the rest after floods).

RESULTS AND DISCUSSION

The samples of soil, sediment and water were collected for the analysis of PCDDs/Fs, PCBs and OCPs. The sampling sites include localities within the chemical factory of Spolana Neratovice and localities from the surroundings (Neratovice, Mlékojedy, Libi, Obíství, Vtruice). Besides these samples they were collected samples from other parts of the Czech Republic. They include both samples from background localities and samples from urbane localities as well.

Figures 1 and 2 show the comparison of 2,3,7,8-substituted congeners of PCDDs/Fs from reference soil and sediment samples collected in the Czech Republic before and after floods 2002 and from the samples collected in the surrounding of Spolana Neratovice

CONCLUSIONS

- Observed contents of PCDDs/PCDFs in Elbe sediments are not higher in comparison to the levels of PCDDs/Fs in industrial regions of the Czech Republic or Europe.
- Similarly the soil contents of PCDDs/Fs are slightly higher than the mean level of contamination in the Czech Republic.
- This investigation confirmed high contamination of some parts of area inside factory and also the existence of other source of PCDDs/Fs contamination. It can be connected with old chlorine production which was stopped in 1975.

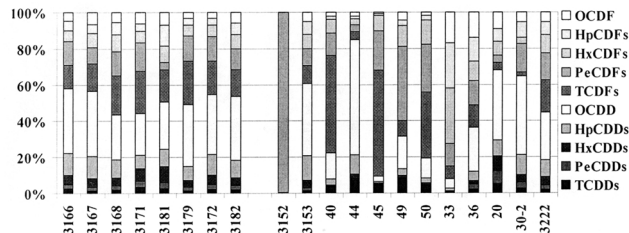


Figure 2: The comparison of 2,3,7,8-substituted congeners of PCDDs/Fs from reference sediment samples collected in the Czech Republic before and after floods 2002 and from the samples collected in the surrounding of Spolana Neratovice

• Beside the PCDDs/Fs contamination, the contamination of environmental matrices by OCPs in the vicinity of the company was detected (soils from the surroundings, water from the area of company and some biotic samples) – which represent more hazardous contamination in this time.

• The determined PCDDs/Fs concentrations in abiotic matrices do not represent acute health risk for human population.

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PROBLEM OF OBSOLETE PESTICIDES IN THE REPUBLIC OF ARMENIA

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Obsolete pesticides represent a great danger for human health and the environment.

No technical, financial and institutional resources are available for the solution of this problem in Armenia. It is known that the problem of obsolete pesticide settlement requires general, universal, systematic, strategic and complex approaches.

In our opinion, the issues of strategic approach involve such basic entries as:

- Overall Inventory/ accounting of obsolete pesticides stockpiles
- Application of appropriate methods of treatment/decontamination
- Implementation of strategy aimed at prevention of obsolete pesticide accumulation.

In this respect top priority is the political will to settle the problem of obsolete pesticides as an urgent measure, as well as to develop and implement national strategic approaches for the solution of this problem, including making detailed inventories.

In Armenia, as a result of the reorganisation performed at large agricultural farms, a collapse-like disintegration of the storage basis took place. As a rule, pesticides subject to utilisation are mixed and exposed to the effect of atmospheric precipitation in ruined storage rooms, which even have no legal owner.

Such stockpiles of mixed obsolete pesticides become local potential sources of pollution of soils adjacent to agricultural lands, ground- and surface waters, atmospheric environment and exert negative effect on the health status of the population.

In Armenia the cases were registered on application of banned preparations that were no man's property. Moreover these chemicals were improperly used (not for their proper purpose): herbicides were applied instead of insecticides and vice versa. This brings forth significant contamination of both the soils of agricultural lands and the crop production.

According to available research data and epidemiological studies performed, confidential correlation dependence was revealed in Armenia between the level of pesticide load and disease prevalence in the general population, especially in rural regions. For example, in regions with the high pesticide load, an increase was registered as to the diseases and pathology of upper respiratory tract, cardio-vascular system, blood-forming organs, especially in cohorts of children and adolescents.

The problem of obsolete pesticides has been urgent for Armenia since the 1980s, when the Government, on the initiative of the State Sanitary and Hygienic Supervision, adopted a decision and in accordance with this approved the Programme for inventory/accounting, withdrawal, and burial of obsolete pesticides. In pursuance of this decision pesticide burial was organised for obsolete agrochemicals in Artashat region of Armenia. According to data available, the volume of buried pesticides made about 512 tons; 50% thereof were organochlorine pesticides, including 192.5 tons DDT.

However, at present the burial is not functioning. It is difficult to define its departmental belonging: who is responsible for its integrity and safety. The state of the burial arises great concerns not only because of lack of due control, but also on account of landslide processes observed in this region recently. All these points are adding to worsening the state of the environment. The problem is still aggravated by the fact that in the vicinity of former pesticide burial, there are summer houses and orchards.

In 2001 the Republic of Armenia signed the Stockholm Convention "On Persistent Organic Pollutants" and in accordance with the National Implementation Plan on POPs in the frames of the Convention, we perform the Inventory/accounting of sources for POPs releases/emissions, as well as wastes containing POPs, including stocks of banned obsolete organochlorine pesticides unfit for use.

The preliminary stage of activity on Inventory of POPs raises a number of problems impeding an appropriate inventory quality:

- Lack of a unified system for organochlorine pesticides management, including lack of a state body responsible for POPs management and raising the problem of POPs as an inter-sectoral, interdepartmental one;
- Complexity to identify potentially toxic chemicals because of lack of a functioning Centre of Register of Potentially Toxic Chemical Substances in Armenia;
- The ownership of pesticide storage sites, lack of registration of such owners, limited access to the storages, and unsatisfactory state of existing storages;

The problem of expired medicine and obsolete chemicals, which can also be classified as hazardous wastes, is of no less importance and priority for Armenia.

Disposal of such compounds must be performed in ecologically sound ways. With this aim, and by joint efforts of the Ministry of Nature Protection and the Ministry of Health, an inventory was made for expired medicine accumulated on the territory of Armenia; the total volume of medicine, according to preliminary data, amounts to several thousand tons. Taking the inventory of expired medicine and chemicals was technically facilitated by the fact that their stocks were clearly fixed in financial account documents of the entities, legal and natural persons, and are on their balance. This circumstance promotes safe storage of these substances prior to their final disposal.

Apart from the expired medicine, an inventory of obsolete pesticides and chemicals is complicated by the fact that

due to the economic reorganisation that took place in Armenia, both the agricultural production and the majority of industrial enterprises were privatised.

As a result of the land reform in Armenia, early functioning system of pesticide centralised supplies and distribution in regions and agricultural entities through the "Armselkhozkhimia" ("Armenian Agricultural Chemistry") was abrogated. At present agrochemicals are imported to Armenia by various commercial organisations and private persons. Due to imperfection of legal/legislative grounds in this sphere one should not exclude the cases of illegal import of expired or banned pesticides.

The stocks of obsolete or banned pesticides that are present at small and middle-size farms very frequently are thrown to nearby open water reservoirs or piled to unauthorized places. Therefore, in Armenia actions are taken to ensure safe storage by the efforts of power structure.

In order to solve the problem of pesticides unfit for use, it is necessary to implement the activity plan according to the following strategic directions:

- Elaboration and realisation of technologies for treatment/decontamination and elimination of unfit/inappropriate pesticides in accordance with economic and technical capabilities of the country;
- Application of technologies especially adjusted for this purposes: high-temperature processing of these substances;
- Application of newest up-dated technologies of chemical, biochemical, biological degradation of element-organic and organo-metallic compounds;
- Development of technologies aimed at short- or long-term isolation of unfit/inappropriate pesticides. Storage with the option to withdraw unfit pesticides as soon as efficient technologies for their treatment or liquidation will be implemented;
- Development and maintenance of a structure to realise main provisions of the action plan;
- Further progress of ecological education and raising the professional level in the sphere of unfit pesticides management;
- Co-operation with general population and public organisations.

In our view, amongst strategic directions of technical character, the creation of a system of special storehouses for safe, controlled storage of unfit/inappropriate pesticides is one of the efficient and easy-feasible ways to minimise the threat of spreading the unfit pesticides in bio-sphere. This method is the most suitable not only from the economical and technical point of view; it is also the least socially dangerous.

Programmes on minimising the risk must contain the following practical measures and actions:

- Identification of presence and localization of unfit/inappropriate pesticides, their evaluation and inventory/accounting. Defining actions and measures on pesticides management at the stages of collection, storing at intermediate store-houses, selection and implementation of technologies for disposal and disposal as such;

- Detailed examination of the revealed unauthorised places of unfit pesticides storage; first of all those places, which have no owners; identification of the owners;

- Control of arranged/controlled store-houses, which have owners but are in threatening condition;

- Determination of an efficient/reasonable complex of technical measures on rehabilitation/ remediation of sites for storage of unfit/inappropriate pesticides, taking into account the ecological risk, as well as economic and technical possibilities;

- Assessment of abilities to isolate unfit pesticides, allotment of sites for places of isolation, start of their preparation (in accordance with the economic possibilities);

- Development of industrial schemes for recycling of unfit pesticides with the aim of their treatment/decontamination and disposal/elimination;

- Development of information analytical system on unfit/inappropriate pesticides;

- Revision, updating and improvement of current legislative and legal background structure required for the solution of the problem on unfit pesticides.

The next issue is a necessity to develop the Plan on realisation of programmes minimising the risk of cumulated unfit /inappropriate pesticides.

Practical realisation of these programmes should be initiated at those places where there are favourable conditions and background to settle the mentioned problem, as well as concern for that.

Attention should be drawn to the necessity to improve legislation in the area of safe pesticide management at all the stages of their life-cycle, taking into account the recommendations of international legislation.

It is also necessary to strengthen the control on illegal import/export of obsolete and non-registered pesticides with the application of mechanisms of the Basel Convention and the Procedure on the Prior Informed Consent of the Rotterdam Convention, as well as to develop preventive measures on exclusion of new accumulation due to exempt false/simulated pesticides.

A major task to be tackled in the sphere of obsolete pesticides is the elimination thereof. In order to achieve this goal it is necessary to perform a complete inventory/accounting of unfit pesticides stocks.

As a consequence of the lack of qualified personnel and modern up-graded laboratories, poor technical equipment carrying out complete inventory of obsolete/banned pesticides, as well as their disposal/elimination would be possible only in case of financial and technical assistance provided by international organisations and donor countries. It is purposeful to establish an appropriate regional fund for the settlement of these tasks.

The following fact signifies to the urgency of the obsolete pesticides problem: this issue was on the list of ecological problems discussed at the meeting of the European Union - Armenia Parliamentary Cooperation Committee (PCC). Discussion of this problem was continued at the next regular meeting of the EU-Armenia PCC, which took place in Yerevan on June 3-4, 2003.

In conclusion, let me express my deepest gratitude to the sponsors for the possibility given the Republic of Armenia to participate in this Forum, my appreciation of the organisers of this event, and to Mr. Vijgen and Ms. Pidlisnyuk in person for the hard and painstaking job to organise the 7th International HCH and Pesticides Forum.

In my view, this Forum is a very successful opportunity

for me as a representative of the Ministry of Nature Protection, Armenia, on the one hand, to address this meeting and render political support for the solution of the problem of unfit/inappropriate pesticides, and, on the other hand, this was a brilliant chance for me to lay open to the public recent data on monitoring and inventory of organochlorine pesticides in Armenia.

THE PROBLEMS OF OBSOLETE PESTICIDES IN GEORGIA

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In Georgia, as in the other former USSR countries, the obsolete pesticides represent a serious ecological problem. Most of these pesticides are persistent organic pollutants which increases this problem. The climate and agricultural plants of Georgia are multi-conditional, which helps spreading and developing injuries and plant diseases that damage agricultural crops. To avoid pests and plant diseases, pesticides of different chemical groups are still in use until today.

The result of the wide usage of pesticides is a high level of environmental pollution. In 90-s levels of some pesticides (for example DDT, GCCG, treflan, etc.) in the soil and water were much higher than the maximum permissible levels. Unfortunately, after 1990 and during the heavy social-economical period, no monitoring of the environmental pollutants was carried out.

It is significant that during the Nineties, the volume of the imported pesticides (between 30,000-35,000 ton/year) was higher than the used volume. As a result, large amounts of obsolete pesticides and other agents for plant protection are accumulated.

These pesticides were placed in the central store "Selkhozimii" and in the stores of former collective and state farms. After breaking-up of the Soviet Union, there was a privatization of properties and their soils and small farms have not been organized in Georgia. The area of such farms is not exceeding 1-1.5 ha. Warehouses of pesticides have been left without any attention. Large numbers of them were destroyed. One part of these obsolete pesticides is turned into conglomerates. The other part was left uncontrolled under the open sky. There is a great risk that these preparations will be washed away by rains and this will cause contamination of the soils and ground-water around the stores, which as a consequence will create a serious risk for both human health and environment.

The existing amount of obsolete pesticides during the year 1995 was more than 2000 ton, but in the following

years this amount was reduced. During the heavy social-economical situation, the stores were robbed and a part of the obsolete pesticides appeared in illegal markets. Nowadays, there are no statistical data, which can show the exact amount of the obsolete pesticides as well as their chemical structures.

The Ministry of Environmental Protection and Natural Resources worked out the program that deals with the handling and utilization of the obsolete pesticides, but due to lack of funds in budget this program was not carried out. In order to solve this problem both financial and technical support are needed.

The landfill located in Eastern part of Georgia (region of Marneuli, mountain on Ialgustkaia) was used for the obsolete pesticides. Since 1986, the landfill has been exploited. Statistical data of "Selkhozchimii" during the period 1976-1985 showed that about 2600 ton of obsolete pesticides was buried. According to the staff of "Selkhozchimii" the obsolete pesticides were eliminated either by burying in concrete boxes, burning or by other means.

The landfill was closed in 1986. Nowadays, the landfill is in a very bad condition. On the surface of this landfill metallic boxes and sacks are found, but the main problem is that these toxic materials are not protected and are accessible and exposed to people and animals. Unfortunately, nobody knows what is happening inside this landfill. We assume that this landfill is the source of pollution and that it is necessary to study the landfill and carry out the actions accordingly.

The official data showed that during the period 2000-2002 the use of pesticides in Georgia recorded 3000 - 4000 tons. Comparing this with what was used during the seventies and eighties, it is obvious that there is a significant reduction due to the difficult economical situation.

Nowadays, the import of some pesticides is prohibited, but illegally they are transported into the country due to the following:

- there is a lot of case of falsification of pesticides by the distributors in Georgia
- the low awareness about pesticides usage;
- lack of monitoring on pesticides usage and
- lack of governmental controls.

In 1998, the Parliament of Georgia passed the law on "Pesticides and Agrochemicals". In 1999 the law of "Hazardous Chemical Substances" was enacted. Draft Waste Law has been approved by the Government of Georgia and sent to the Parliament for final approval.

In 1999, Georgia joined the **Basel Convention** in the 2001 Georgia signed the Stockholm Convention. The program on inventory of persistent organic pollutant (POPs) and a national plan in the framework of the Stockholm Convention was worked out. The program was approved by Global Environment Facility (GEF) and was signed up by Ministry of Environmental Protection and Natural Resources. The executive agency is **UNDP (United Nations Development Programme)**. The program will begin soon.

Due to the solving abovementioned problems it is necessary to carry out next steps:

- Inventarisation and identification of obsolete pesticides
- Definition of the scale of environmental pollution created by obsolete pesticides especially in soil and ground-water;
- Working out the national plan for the destruction or final disposal of obsolete pesticides and identification is the first step to carry out;

- It is necessary to realize step by step the final destruction of obsolete pesticides by using environmental sound methods;

- Study the conditions of the landfills;
- Developing a system of monitoring and improving the governmental control in the use of pesticides;
- Public awareness for the use the pesticides;
- Using the international recognized methods against the harmful insects and
- Improving the legislation base and make its harmonization with the EU Standards.

Taking into account the economical situation of Georgia, it is very difficult to fulfill aforementioned actions without financial support from of the international organizations and the donors. We hope that international organizations will show strong interest in solving these problems.

PROBLEMS RELATED TO OBSOLETE PESTICIDES STOCKPILES IN THE REPUBLIC OF MOLDOVA

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Although there are some signs of improvement of the situation, the problem of environmental pollution and first of all soil and surface waters contamination with pesticides in the Republic of Moldova still persists.

Despite the tendency of a regular reduction of the obsolete pesticides stocks during last years, their general number remains very high, a fact that concerned the Government and large public.

The problem is caused by a set of factors, such as:

1. The prevalence of the agricultural sector and industrial processing of agricultural products in the national economy.

2. The presence of wide areas of fruit and vegetable plantations, which are the source of raw materials for industrial processing of agricultural products, but which need frequent treatment with chemicals.

3. Moldova as a part of the former Soviet Union served as an experimental base in using chemicals in the agricultural sector.

Popular in that time the term «chemicalization of agriculture» obtained a threatening expression. The intensity of the utilization of pesticides in Moldova in the 80s exceeded average world indexes. In that time more than 50,000 tons of pesticides were imported every year, which made up 20-25 kilograms / hectare in active substance. Since 1990 the significant use of pesticides has been reduced in the country. It was favourable to the environmental situation in the agricultural sector.

The evident decrease of pesticide use in the last years led to considerable minimization as a component of natural resources and agricultural products. The results of the ecological and sanitary bodies' control show that generally the agricultural products are not polluted with pesticides. The excess of the permissible norms of pesticides content in agricultural products was found less than 1% in the analyzed samples.

The investigations, which were implemented on 64 areas, proved that soil pollution with chloroorganic pesticides is not significant and on most of the territory the main

Year	Till 1990	1990	1992	1994	1996	1998	2000	2002
Pesticide load (kg/ha) of active substance	15-20	6.4	4.6	2.1	1.7	1.3	1.1	1.0

Table 1: The dynamics of pesticide loads per one hectare of agricultural used area

concentration of DDT and Hexachlorocyclohexane is lower than maximum permissible concentrations. Insignificant exceedance of maximum permissible concentration was found only in some areas. There wasn't found any other residual concentrations of others pesticides in soil.

4. Another factor was the low level public acknowledgment of the consequences of exceeding the standards of use and the rules of application of the chemicals. This contributed to the development of the idea "the more pesticides are used – the better is the plant protection and the higher is the crop (harvest)".

5. Also the Centralized supply system and the subsidized cost of pesticides contributed to the formation of the non-used pesticides stocks, which led to the fact that more pesticides were imported than was needed in fact.

The lack of strict laws in that time, regarding pesticides import control, transportation, storage and use, and the lack of real price policy on pesticides as well, led to the accumulation of a large number of unused and prohibited pesticides.

In 1977 a special landfill site was built and operated in the South of the country near Cismichioi village. This was done to solve the problem of pesticides wastes elimination. From 1977 to 1987, about 4,000 tons were buried there. Owing to the fact that this landfill site is closed and conserved, the accumulation of unused and prohibited pesticides took place on numerous depositories of collective farms.

In accordance with official data of inventories, which were held by Ministry of Agriculture and Food Industry, the stocks of these pesticides wastes varied in last years from 2628 tons in 1997 to 1712 tons in 2002. The 2002 inventory indicates that the stocks of these pesticides are at 344 depositories.

Besides the above-mentioned pesticides there are other pesticides, which were forbidden according to the Stockholm Convention and Aarhus Protocol and international measures for prevention, spread and consecutive elimination of these pesticides should be worked out: toxaphene - 131 t, HCH - 21.7 t, and a small quantity of DDT and heptachlor (according to the results of the inventory).

In most cases, because of bad stocktaking and stockholding, chemicals are not labeled, the packing is in bad state and the products are mixed. That is why their identification requires significant material and financial expenditures.

The situation is complicated because, as a result of organizational confusion and forced agrarian reform after the liquidation of big collective socialistic farms and the establishment of the private sector, the majority of storages remained without owners and were destroyed. Further a

significant part of stored pesticides remained in open air and were under the influence of atmospheric precipitation and wind. Consequently these deposits turned into sources of environmental pollution with chemical toxic substances. Because these wastes were not protected they became accessible to people, which led to uncontrollable utilization and dissemination. The Ministry of Ecology and the Ministry of Health of Moldova assess this situation as extremely dangerous.

In 2002, the State Ecological Inspectorate performed the assessment of over 20 of such ruined deposits, which showed that at the distance of 5 m from deposits the contents of chloroorganic pesticides in soil exceeded maximum permissible concentrations (MPC) in 9 times, and at the distance of 150-200 m the exceedance is from 3.5 up to 7 times.

Taking this into account, it is obvious, that the main urgent problem is environmentally safe removal of pesticides at 344 stocks, which are not suitable for usage. Several times the Government of the Republic of Moldova adopted measures for removal of pesticides wastes. For example the centralized storing of pesticides wastes, which was dispersed all over the territory, was planned to one single warehouse per rayon. The warehouses had been furnished and were ready to receive the waste of each rayon.

However, every time when these measures were planned they could not be implemented because of two reasons:

1. Financial problems. For implementing the whole number of actions, including: the carrying out of laboratory chemical researches for identification the chemical structure of pesticides stored in each deposit; the repackaging and transportation for their centralized storage; the working out of technological processes and technological equipment for incineration; the determination the chemical content of products, which were received as a result of their incineration and their possible impact on environment -- required significant financial resources, which our Government, unfortunately, could not find.

2. The resistance of population is the most difficult problem to solve in Moldova. Under the conditions of a high density of the population, with about 130 people on one square kilometer, in small remote settlements, from 0.5 km up to few kilometers from each other, it is very difficult to establish the centralized deposits and technological installations for pesticides incineration. In the case of application of centralized pesticides wastes incineration – the population expresses its anxiety concerning the aspects of the exploitation of these installations, such as:

- The character of storing pesticides and incinerated pesticides;

Year	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002
Obsolete pesticide stocks (thousand tons)	1225	1284	1159	1151	2628	2627	1850	2103	1963	1712

Table 2: The number of unused and prohibited pesticides stocks (thousand tons)

- Possible accidents and cases of emergency, as a result of which the emissions of dangerous chemical substances are possible;

- Pesticides leakage during transport. In case of a centralized storage and incineration the population starts to think: Why should we do it here? And why should we suffer for all?

It is obvious, that the resistance of the population will be less, if mobile installations are used, in which the period of incineration is limited and consequently only the local wastes are incinerated. This is psychologically very important, because in such circumstances the population will be aware of the necessity of eliminating their own wastes.

Unfortunately, the use of other neutralization pesticides wastes methods, besides incineration, under our conditions is practically impossible.

The establishment of landfill sites with underground pesticides burial is less used, because of the high density of populated areas. The same problems and experiences with the landfill exploitation for burying the pesticides wastes exist in the South of Moldova, which I mentioned before and which causes constant concern of population.

During the period of 10 years exploitation, about 4,000 tons of different pesticides, among which are 654 tons of DDT, were buried in the landfill. In 1999-2000 in the framework of the TACIS Programme there were performed researches, which confirmed that at present this landfill site has no harmful impact on the environment. It is indispensable

to take into account that after some period the depressurization of the landfill and particularly of its cover layer can take place, which can cause the geological pollution, soil pollution, surface and groundwater pollution. This again can cause an environmental catastrophe. That is why these pesticides wastes must be eliminated urgently in the near future.

CONCLUSIONS:

1. The paramount problem is the neutralization of 1,712 tons of unused and prohibited pesticides located in 344 deposits, which are the source of environmental pollution with high danger.

2. 4,000 tons of pesticides wastes buried in the landfill in the South of Moldova near Cismichioi village: permanent monitoring needed.

3. Taking into account the demographic and natural conditions of the Republic of Moldova, the most realistic way of pesticide wastes elimination is the high temperature incineration in the mobile installations directly at places, where pesticides are located.

4. The Republic of Moldova has financed the start of the works for repackaging and

centralized storage of obsolete pesticides, in a volume of 2 mill. MDL in 2003 and plans the same for 2004, but will need additional money for final elimination. Therefore we will rely on that financial support from international organizations and donor-countries. We are also ready for close cooperation without delay in solving this problem.

STATUS AND PROBLEMS OF OBSOLETE PESTICIDES IN UZBEKISTAN

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WHAT IS THE PRICE FOR A GLASS OF PURE DRINKING WATER?

Uzbekistan has been specialized in cotton production since Soviet times. The area where cotton is produced is about 1,6 million hectares, and it is still the main growing culture in the country. The reason of it is very simple - cotton remains the main source of income giving "real money".

Defoliation is carried out before harvest and is conducted straight from planes, spreading poisonous clouds of pesticides right on the heads of cotton pickers. Women and children are the main cotton pickers. 43 per cent of soils in Aralski Krai are contaminated with chemical fertilizers, pesticides and phenol. Within the Khorezm

region a vast territory from Urgench to Mangit is contaminated with pesticides where the DDT content in soils exceeds maximum concentration limit 20-24 times, and in the area of old abandoned aerodrome locations 28-35 times.

In the Republic of Karakalpakstan on the left side of Amudaryja, Khodjeili, Shumanai, Kanlikul district intensive contamination is determined (maximum concentration limit more than 15 times). In the vale of Zarafshan River, Dzhizak province contamination with nitrates, pesticides and strontium maximum concentration limit is characteristically 2-6 times, and around storehouses and aerodromes 5-8 times.

According to data of Glavgidromed RUz, contamination of farming lands and water resources of Tashkent and Ferghana regions does not fall despite of prohibition in usage of DDT that was made in 1983. For example, the level of DDT concentration in soil of "Nurobod" Ferghana region Oltinarik province is very high and reaches 22-24 times the maximum concentration limit. In Andijan region it amounts to 3-5 the maximum concentration limit. The average content of defoliant residue exceeds its norm in every region and in Ferghana region



Photo 1: General view of pesticides burial (more than 20,000 tons) located in Djizak province, Egizbulok village, RUz.



Photo 2: Soil subsidence as a result of sharp phreatic rise at the site of pesticides burial

5-6 times. According to Goskompriroda data, the most contaminated areas are former aerodromes of farming aviation. The total quantity is more than 460, predominantly with contamination of chlorine-organic pesticides. For example, in “Karasu” farming Angor region it is 106 times the maximum concentration limit, in “Samarkand” farming Pastdargom region 153 times the maximum concentration limit, in “Uzbekistan” Kumkurgan region 253 the maximum concentration limit, and in “Turaev” Pastdargom region 379 times the maximum concentration limit.

Farming aerodromes of Gijduvan, Karaulbazar, Peshkun and Bukhara regions are contaminated with residue chlorate magnesium between 3-6 times the maximum concentration limit; with nitrate and fluoride from 2-3 times the maximum concentration limit in farming aerodromes of Usman Yusupov, Guzar and Kasbin regions. Farming aerodromes of Zafarabad and Farish regions are contaminated with phosphorus 2-3 times the maximum concentration limit. The area around the central pesticides storehouse in Dzhalkuduk region is contaminated with chlororganic pesticides between 4-27 times the maximum concentration limit.

The situation remains rather acute until today. As an example, citizens of Egizbulok village, in Dzhizak province applied to the center “Armon” about environmental contamination with toxic pesticides disposed in 1987.

The old storehouse, located on the territory of 5 hectares, became useless and demands repackaging of barrels with pesticides and the carrying out specialized work on their proper storing. Table 1 contains the list of pesticides stored in Egizbulok village. As is shown, there are extremely dangerous specimens.

GHCG

toxaphene

Heptachlor

The situation is getting complicated because of environmental ignorance of the population, who digs out the store-

house and use pesticides for extermination of rats and cockroaches. They even do not suspect that they can be poisoned by fatal dose. See also Photos 1 and 2.

Examinations show that deficiency of iodine in water results in immune system changes, appearance of cretinism elements, sclerosis and the whole number of other diseases. Following the World Health Organization data frequent catarrhal diseases, beriberi, reduction of mental ability, and anemia at children are fixed in regions with iodine deficiency. This is only the lack of iodine.

AND WHAT IF CONTENT OF PESTICIDES IN WATER EXCEEDS TEN TIMES?

Uzbekistan is the world’s largest consumer of chemicals and pesticides for the last 50 years. Cotton has become a national tragedy. In “good, old, soviet times” during “the battle for white gold” a lot of people died. Slave labor of children, old people, and women in the fields was recompensated with the rain of pesticides dropped from airplanes. More than 70 per cent of the population (15 million.) resides in the rural area that suffered from defoliation. Isn’t it a genocide against the own nation? “Red” sank into oblivion and cotton has been still fertilized with defoliant. Uzbekistan ratified Rotterdam Convention undertaking obligation of presenting complete information to population concerning certain dangerous chemicals and pesticides.

Strategy of sustainable development includes timely prevention of possible environmental threats leading to tension. It seems to me, efforts of the governmental bodies alone are not sufficient for positive resolution of environmental problems. Half the battle lies in consolidation of governmental, public, and business sectors.

WHO CAN PROTECT THE RIGHTS ON HEALTHY ENVIRONMENT?

Only the population itself is obtaining access to legal knowledge. Citizens all together and each individual wishing to protect themselves and children from degeneration.

Chemical denomination	Quantity (in tons)
Dendrabacilin 30 billion	5.45
Kelthane	40.3
Trichlorfon	39.704
Copper oxychlorid	2.0
Copper trichlorophenilate	6.0
TMTD 80%	3.16
Propionate natrium	34.675
Omayt	0.1
Granosan	1.07
Phasonol	0.95
BIP	1.148
Kelthane	1.3
GHCG 12%	800.0
GHCG 25%	400.0
Preparation 30	120.0
Polydaphen	200.0
DDT Emulation	240.0
DDT paste	60.0
DDT sp	80.0
Zineb	39.7
BI-58	11.0
Soil	30.0
Pentatiuran	36.5
Prep SK-9	21.2
Pentachloronitrobenzol	55.0
Chlorethanol «Kelthane»	42.7
Dentrobocelin-100 billion	63.0
TMTD	16.5
Pretazin	0.979
Amine saline	38.7
Saccin acid	347.0
Phosmomid	0.355
Ustiks	0.8
Prep	0.250
Uephen	0.07
Basta	0.45
Sumi-8	0.24
Kataran	0.435
Nitrophen	0.54
Promethrin	0.55
Total	2741.826

Tare	Quantity, pieces
Containers of nitrophen	2476
Containers	185
Palettes	4860
Apraktan	10 000
Containers of kelthane	1790
Barrels with prap-30	971
Barrels with trichlor	223
Barrels with other chemicals	240

Table 1: Toxic chemicals content of the tailing pit in Egizbulok village, Farish district, Dzhizak province.

WHAT IS NECESSARY TO SOLVE THIS ISSUE?

Access to justice is complicated; information on impact of pesticides on health of population is practically not published in Mass Media.

Aggravation of environmental conditions can be explained not only by economical instability, and low legal education of population in the field of environmental rights protection, but insufficient effectiveness of current legislation. It is necessary to work out:

- Mechanisms and tools of social control over realization of ratified international Conventions and public participation
- System of regular informing the population on impact of pesticides on health of population
- Increase the number of treatment plants for pesticides destruction that have become worthless and forbidden for use
- Creation of areas available for pesticides destruction in Ferghana, Dzhizak and Surkhandarya provinces.

SUMMARY

OF SESSION ON MONITORING AND RISK ASSESMENT AT STOCKS, IN SOILS, GROUNDWATER, PLANTS AND IN HUMAN BODIES

Ivan Holoubek and Ivan Atanasov

MONITORING/RISK ASSESMENT:

- Data reach, information poor
- The simplicity is beautiful - simplicity leads to a considerable number of advantages including sustainability
- The arrangements of monitoring programme must have a high expectation of being sustainable
- Many countries will not have the laboratory analytical capacity to support the effectiveness monitoring programme approach
- Even if capacity building resources to provide the required infrastructure can be made available, it is very doubtful that the level of work required would be sufficient to sustain that infrastructure over time
- The quality assurance and quality control implications necessary to ensure the comparability and harmonization of the monitoring programmes on the regional or national levels
- Lack of data comparability will prevent meaningful comparison of national trend assessments
- Utilization of existing regional and national programmes and mechanisms is possible
- This approach could be cost effective, since it would primarily use the existing EC inventory of analytical laboratory infrastructure already linked through established data comparability networks
- Data from monitoring are useful source of information for exposure assessment as a one from the basic components of risk assessment
- For risk assessment is suitable to combine chemical monitoring with ecotoxicological monitoring, bioassays and biomonitoring

THE UNEP / GEF PROJECT REGIONALLY-BASED ASSESSMENT OF PERSISTENT, TOXIC SUBSTANCES – EURO- PEAN REGIONAL REPORTS

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1. INTRODUCTION

Following the recommendations of the Intergovernmental Forum on Chemical Safety, the UNEP Governing Council decided in February 1997 (Decision 19/13 C) that immediate international action should be initiated to protect human health and the environment through measures which will reduce and/or eliminate the emissions and discharges of an initial set of twelve persistent organic pollutants (POPs). Accordingly an Intergovernmental Negotiating Committee (INC) was established with a mandate to prepare an international legally binding instrument for implementing international action on certain persistent organic pollutants. These series of negotiations have resulted in the adoption of the Stockholm Convention in 2001. The initial 12 substances fitting these categories that have been selected under the Stockholm Convention include: aldrin, endrin, dieldrin, chlordane, DDT, toxaphene, mirex, heptachlor, hexachlorobenzene, PCBs, dioxins and furans. Besides these 12, there are many other substances that satisfy the criteria listed above, for which their sources, environmental concentrations and effects are to be assessed.

There is a need for a scientifically-based assessment of the nature and scale of the threats to the environment and its resources posed by persistent toxic substances that will provide guidance to the international community concerning the priorities for future remedial and preventive action. The assessment led to the identification of priorities for intervention, and through application of a root cause, analysis was attempted to identify appropriate measures to control, reduce or eliminate releases of PTS, at national, regional or global levels. Based on this approach, the GEF and UNEP

Chemicals prepared the project “Regionally Based Assessment of Persistent Toxic Substances”.

The basic project topics were:

1. Identification of major sources of PTS at regional level;
2. Impact of PTS on the environment and human health;
3. Assessment of trans-boundary transport of PTS;
4. Assessment of the root causes of PTS-related problems, and regional capacity to manage these problems;
5. Identification of regional priority PTS-related environmental issues; and
6. Identification of PTS-related priority environmental issues at global level.

The outcome of this project will be a scientific assessment of the threats posed by persistent toxic substances to the environment and human health. The activities to be undertaken in this project comprise an evaluation of the sources of persistent toxic substances, their levels in the environment and consequent impact on biota and humans, their modes of transport over a range of distances, the existing alternatives to their use and remediation options, as well as the barriers that prevent their good management.

To achieve these results, the globe is divided into 12 regions: The Arctic, North America, Europe, Mediterranean, Sub-Saharan Africa, Indian Ocean, Central and North East Asia (Western North Pacific), South East Asia and South Pacific, Pacific Islands, Central America and the Caribbean, Eastern and Western South America, Antarctica. The twelve regions were selected based on obtaining geographical consistency while trying to reside within financial constraints. Region III – Europe – consists of 29 countries in Western, Northern, Central and Eastern Europe, the member countries of EU and many countries with transition economies. Region III has a lot of information concerning the sources and environmental levels of PTS, but geographic distribution of the available data is not equal for all parts of the Region, here the situation is better in some EU and Central European countries.

2. SOURCES OF PTS

Persistent Toxic Substances (PTS) can be introduced into the environment via numerous sources and activities. Point and diffuse sources include releases from industrial and domestic sites, traffic, waste disposal operations such as incinerators and landfills. Secondary sources include the spreading of sludge on land and remobilisation of previously deposited compounds from soils and water bodies. Some sources are capable of regulation (such as industrial point sources) while other diffuse emissions represent unregulated and/or difficult to regulate inputs (fugitive releases from landfills, domestic open burning of waste).

During the last decade a large amount of progress has been made in the production of atmospheric emission inventories of several PTS compounds within Europe. However there is still a lack of comparability in inventories produced by various organisations for the same compound group and this reduces transparency when comparing or compiling inventories. Improved emission inventories for

PTS have become increasingly important as emission or source-driven fate models for regional and global scales are developed. Inventories serve as useful information for decision-makers in order to reduce the impact of these pollutants on the environment.

Source inventories represent a crucial step in developing appropriate risk control strategies for PTS. Using an inventory of releases to air, water or land it is possible to rank sources in order of importance and so target source reduction measures effectively and incorporate effective risk reduction measures.

During the last two decades there has been a growing interest within the environmental research community to understand the fluxes, behaviour, fate, and effects of PTS compounds. Various studies and assessments of PTS in the environment have been carried out by several international organisations, such as United Nations Environmental Programme (UNEP), the United Nations Economic Commission for Europe (UN ECE), the World Health Organisation (WHO), the Nordic Council of Ministers, the Paris and Oslo Commissions, the Helsinki Commission, and the Great Lakes Commission, as well as the Arctic Monitoring and Assessment Programme (AMAP).

CONCLUSIONS

- Within the Region as a whole there is a large amount of data relating to industrial point source emissions to the atmosphere. Sources to air of well studied compounds such as PAHs, PCBs, and PCDDs/Fs are generally well characterised and inventories have been calculated and updated regularly via EMEP. Due to restrictions on the manufacturing and more stringent control of releases, emissions from primary sources have been declining during the last 20 years. Understanding of secondary source inputs and the potential for environmental recycling of individual compounds continues to be limited and few measurements are available.

- Obsolete stocks of pesticides represent a potential source of PTS material particularly within the Central European Countries and Newly Independent States. Exact quantities and components of the stockpiled wastes are unknown at present but quantities are thought to be in excess of 80,000 t.

- For the compounds of emerging concern (e.g. PBDEs, chlorinated paraffins) emission sources to all environmental compartments are very poorly characterised, few formal inventories have been established and there is limited understanding of the principal contemporary source categories. For PBDEs, evidence of increasing concentrations in human tissues from Sweden would suggest that emissions into the Region have been rising during the last 20 years.

- Unlike sources to air, sources to land and water are very poorly quantified for all the PTS compounds.

- Prioritisation of source inputs within the Region as a whole highlights the fact that the following compounds represent ongoing releases in the Region which are of most concern with respect to the environment and health:

- Hexachlorobenzene
- PCBs
- PCDD/Fs
- PCP
- PBDEs
- Chlorinated paraffins

3. ENVIRONMENTAL LEVELS, TOXICOLOGICAL AND ECOTOXICOLOGICAL CHARACTERISATION

Levels and trends

The first part of the Regional Report deals with the environmental levels and trends. The relative spatial and temporal variations in environmental concentrations of PTSs are briefly described. The following sections describe ecotoxicology, toxicology and human exposure to PTS in Region III.

Conclusions

- Region III has a lot of information concerning environmental levels of PTS, but geographic distribution of the available data is not equal for all parts of the Region – some EU and Central European countries witness a better situation.

- Very good and traditional monitoring systems concerning also PTS exist (EN ECE EMEP, OSPAR, HELCOM), which are oriented towards air and deposition (EMEP), and seas (OSPAR, HELCOM); some new are ongoing (Caspian Sea, Black Sea). As far as rivers are concerned, monitoring is mainly realised at the national level, but a lot of multinational or regional activities already exist (Rhine, Danube).

- The measurements of PTS levels in some other compartments such as lakes, soils or vegetation is partly performed based on the international programmes (IM EMEP), national monitoring programmes (soils) or pilot or research projects (biota, lakes). Human exposure is measured and studied at European levels (activities of WHO Europe) and very frequently at national levels.

- Although monitoring indicates that the loads of some hazardous substances have been reduced considerably over the past ten years especially in the Baltic Sea region, problems still persist. Comprehensive knowledge about the impact of most available chemicals, and their combinations, on human health and the environment is still lacking.

- The increasing number of these man-made substances is a matter of concern and calls for the application of the precautionary principle. On the other hand, other waters such as the Black Sea or Caspian Sea still have a lot of heavily contaminated sites, where petroleum hydrocarbons and phthalates are the dominant organic contaminants of the Caspian Sea. Only traces of persistent organochlorines were detected in the Caspian seals (highest link of the food chain). But also the level of contamination of the Caspian Sea decreased significantly during the last 10 years.

- The loads of many substances have been reduced by at least 50 % since the late 1980s - mainly due to the effective implementation of environmental legislation, the substitution of hazardous substances with harmless or less haz-

ardous substances, and technological improvements.

- In former Communistic countries reductions have been mainly due to fundamental socio-economic changes.

- The OCPs are no longer in use, have never been used, or have even been banned within the Region III. But one serious problem that remains is that in some countries various obsolete pesticides still remain in temporary storage, awaiting suitable disposal.

- Polychlorinated biphenyls (PCBs) are no longer produced or used in new ways. Inventories are still being carried out in CEECs. Following an analysis of the legislative situation throughout the CEE part of the Region, and the current uses, stockpiles and releases of PCBs measures have been proposed to ensure their safe handling and to reduce releases of PCBs from existing equipment.

- As a result of former production, long-time and widespread use and also long-range transport from other parts of the Globe, OCPs, PCBs, PCDDs/Fs and PAHs and also some newer PTS are found in all environmental compartments including remote high mountain European sites, but principally decreasing trends are observed.

- In this context, it is important to remember that a lot of countries of the Region, such as the UK, Germany and others, have a long industrial history, involving combustion activities in the form of wood and coal burning. For example in the UK, over 65 million tonnes of coal were burned each year nationally in the 1850s. The smelting of metals and the production of iron and steel also have a long history in the UK and the rest of Europe, processes known to have significant PCDDs/Fs emissions. It is important to remember that the history of PCDDs/Fs environmental impacts in the UK and Europe may therefore not be mirrored in other regions of the world.

- Several studies reported that PCDDs/Fs levels in the air are declining in urban/industrialised centres. These trends are observed in Western Europe and are believed to be largely due to emission abatement actions taken in the early nineties. The decline of PCDDs/Fs levels in the atmosphere resulted in a decrease of these compounds in “atmospherically impacted” media such as vegetation, cow’s milk and meat products. Moreover, the human dietary intake of dioxins and furans dropped by almost a factor of two within the past seven years.

- Analyses showed a decrease in the concentrations of the PAH compounds in the particle-phase in the ambient air during the second part of the 1980s. This is a result of the fact that cars equipped with catalyst engines became mandatory in 1991. Also improvement of the fuel and the increased use of district heating contribute to this trend. As far as the last 10 years, and the annual average concentrations of PAHs seem to stagnate due to a permanent increase in motorised traffic on the one hand and a better combustion technology and an increase in the use of natural gas for domestic heating on the other hand.

- A relatively worse situation can be observed in the towns in the former Communistic countries, where the number of cars increased dramatically after the political changes. The same problems exist in all larger cities in CEE countries

after the political changes – extremely high increase in town traffic and decreasing contribution from former industrial sources as the result of declining productions.

Ecotoxicology of PTS of regional concern

This chapter describes the effects in organisms other than humans, which have been proved for region Europe III by means of special research. The term “ecotoxicology” will be used to discuss the effects of persistent toxic substances (PTS) on both the aquatic and terrestrial biota.

Conclusions

- Analysis of the observed ecotoxicological effects of PTS on birds, mammals and fish in Europe has shown that although a wide number of laboratory and manipulated in situ studies with various organisms and effects were conducted and are documented in literature, these data still have to be carefully and critically evaluated.

- On one hand, the controlled toxicological laboratory studies with individual compounds or carefully prepared mixtures usually allow clear dose-response causality between chemical exposure and observed effects to be defined.

- On the other hand, laboratory tests alone seldom adequately describe what is likely to occur in the environment. The often complex and subtle effects of chronic, low-level environmental exposure to PTS are less well understood.

- In the environment, the universal exposure of organisms to low levels of a wide range of chemical contaminants makes it extremely difficult to ascribe an observed effect to any particular one of them. There is also the possibility that, in the environment, toxic substances in combination may act additively, antagonistically or synergistically.

- PTS can act via different mechanisms and cause various adverse effects in wildlife. Mechanisms causing ecotoxicological effects include non-specific toxicity (narco-sis) and more specific mechanisms, such as aryl-hydrocarbon receptor (AHR), mediated toxicity, steroid receptor-dependent effects, metabolic activations, immune suppression and neurotoxicity.

- The assessment of priority of PTS, included in the list of the Stockholm Convention, has been performed by scoring them on the basis of data available in the Region Europe-III.

- The second group of ecotoxins, which were mentioned in the Stockholm Convention, was also scored.

Human effects of PTS of regional concern

Many environmental epidemiological studies indicate that correlations do exist between chemical contamination and observed human health effects. To evaluate critically the adverse effects of individual PTS, it is necessary to compare data derived from experiments with the laboratory animals, the results of epidemiological studies due to accidental or occupational exposure, as well as the effects observed for the average population.

It is very difficult to elucidate cause and effect relationships between human exposure to low levels of a PTS in the

environment and the particular adverse health effects, not least because of the broad range of chemicals to which humans are exposed at any one time. The measurable residues of PCBs, dioxins and various organochlorine pesticides present in human tissues around the world and contamination of food, including breast milk, is also a world-wide phenomenon.

Evidence of low-level effects of PTS on humans is more limited than those of wildlife but is consistent with effects reported both in exposed wildlife populations and in laboratory experiments on animals. This is why the data from „hot-spot“ accidental events or occupational exposures can help to formulate the safety values for PTS. Trying to elucidate the toxicological effects of PTS, one has always to remember the many confounding factors affecting human health (lifestyle, dietary habits), which are often very poorly evaluated.

Concluding the general introduction, it is worthwhile to mention that WHO came to the conclusion, that „where levels of some PTS in breast milk approach or slightly exceed tolerable levels, breast feeding should not be discouraged since the demonstrated significant benefits of this practice greatly outweigh the small hypothetical risk that POPs may pose“. This conclusion has been supported by the report of AMAP, the authors of which suggest that consideration should be given to developing dietary advice to promote the use of less contaminated traditional food items, which will also maintain nutritional benefits.

Conclusions

- Analysis of the results of environmental epidemiological studies shows that correlations do exist between the chemical contamination of air, water and soil and human health. To elucidate the particular effects of individual toxicants (genotoxicity, estrogenic effects, carcinogenicity, neurotoxicity, immunotoxicity, etc.) it is important to compare the above-mentioned results with the data obtained from experiments with laboratory animals.

- The assessment of priority PTS, included in the list of the Stockholm Convention, has been performed by scoring them on the basis of data, available in the Region Europe-III.

- The second group of toxicants, which were mentioned in the Stockholm Convention, was also scored.

Human exposure to PTS compounds in Region III – Europe

The persistent bio-accumulative properties of PTS substances mean that they have the capacity to transfer through terrestrial and aquatic food chains and accumulate in human lipids. As omnivores we occupy a top position in terrestrial and aquatic food chains and as a result consume a high proportion of food in which persistent lipophilic compounds will have effectively biomagnified. Once ingested, PTSs sequester in body lipids, where they equilibrate at roughly similar levels on a fat-weight basis between adipose tissue, serum, and breast milk.

It is possible to document three distinct types of human exposure to PTS compounds:

- **High-dose acute** exposure: typically results from accidental fires or explosions involving electrical capacitors or other PCB-containing equipment, or high dose food contamination.

- **Mid-level chronic** exposure is predominantly due to the occupational exposure, and, in some cases, also due to the proximity of environmental storage sites or high consumption of a PTS-contaminated dietary source, such as fish or other marine animals.

- **Chronic, low-dose** exposure is characteristic for the general population as a consequence of the existing global background levels of PTSs with variations due to diet, geography, and level of industrial pollution. Low level and population-wide effects are more difficult to study. People are exposed to multiple PTSs during their lifetime and all individuals today carry detectable levels of a range of PTSs in their body lipids.

Over the last 10-15 years, as interest in exposure to these compounds has increased, there have been numerous surveys of both typical ‘background’ levels in the population and also small surveys of occupationally exposed individuals whose body lipids contain elevated concentrations.

Compounds are most often monitored in human milk, serum and adipose, although milk monitoring is far more widely practiced due to the relative ease of sample collection. Milk not only provides evidence of maternal exposure to contaminants, it also provides information to assess risk to breast-fed infants. Contaminants in breast milk for example increase with maternal age and decrease with the number and duration of lactation periods (e.g. TCDD levels in breast milk decrease roughly 25% after each successive breast-fed child). The most popular compounds for analysis include the OC pesticides and PCBs.

Numerous analyses have now been made of PCBs in samples of human milk from the general population within the region. Countries with a long history of human tissue sampling - from the early 1980s - include the Netherlands, Sweden and Germany. Within the Central European Countries, Slovakia, the Czech Republic and Poland also have a sizeable database of information spanning the last 10-15 years. Standardised collection and analytical protocols now exist for analysing many PTS compounds in breast milk in these countries, in addition to tissue banking facilities. For example, between 1986 and 1997 over 3,500 milk samples were analysed in Germany for a range of organochlorine compounds. Far fewer analyses of human samples have been made for PCDD/Fs, principally due to the high cost. As a general rule, travelling eastwards within the Region, the number and size of data sets for all compounds reduces significantly.

Evidence from market basket surveys of principal foods and food groups suggests that exposure to many of the classical PTS compounds via food is very similar

throughout the Region. This is also supported by the extensive movement of food products throughout Europe, providing many consumers with a 'European' average food basket of produce. To a large extent personal choices in food preferences will ultimately control our intake of persistent compounds throughout life. Since aquatic food chains are subject to a greater loading of many pollutants than terrestrial ones, individuals who consume fish and seafood obtain an appreciable proportion of their annual intake via this route. For example, fishermen on the east coast of Sweden who have eaten fatty Baltic fish (herring and salmon) almost daily were found to have roughly twice the blood levels of DDT, PCBs and dioxins than people with a more average fish intake.

European exposure to dioxins via food has declined considerably during the last decades. This is due to successful efforts that have led to the reduction of many known dioxin sources. Today the estimated intake by the European population of PCDDs/Fs and non-ortho PCBs, expressed as WHO-TEQs, is 1.2-3.0 pg.kg⁻¹ bw.day⁻¹. Since the 80ies various tolerable daily intake „recommendations“ have been used, and for many population groups, such as new-borns and consumers of high amounts of fish, these recommendations have been exceeded, and still are. Recently a tolerable weekly intake (TWI) of dioxins, furans and non-ortho PCBs, corresponding to 14 pg WHO-TEQ.kg⁻¹ bw, was set by the EU Scientific Committee on Food (SCF).

The SCF has, as of 2002, established maximum limit values for dioxins and furans in consumer food on the European market in order to reduce the overall dioxin contamination of the food chain, and the exposure of the European population. The goal is to have a 25 % decline in the exposure by year 2006. The WHOPDDs/Fs-TEQ maximum limits, based so far on the concentrations of PCDDs/Fs only, are set for foods such as meat, fish, poultry, dairy products and oil and fats and range from 0.75-6 pg.g⁻¹ lipid. With one exception the WHOPDDs/Fs-TEQ maximum limit is set on lipid basis, namely for fish. For fish the EU limit is 4 WHOPDDs/Fs-TEQ.g⁻¹ fresh weight.

The absolute and relative contributions of PCDDs/Fs and non-ortho and mono-ortho PCBs to the total WHO-TEQs of six foods – chicken, beef, butter, human milk, salmon and cod liver from Northern Europe, were determined and compared to the current EU limit values. For all foods studied, PCBs contribute to more than 50% to the total WHO-TEQ. For cod liver the contribution of PCBs to the total WHO-TEQ is high at more than 80%. Sum TEQ levels in the salmon and cod liver reflects the relatively highly contaminated aquatic food chain.

Conclusions

- In summary, human exposure to PTS compounds is dominated by intake via terrestrial and aquatic food products which have high lipid content and have been subject to bioaccumulation within agricultural food chains such as

milk, meat, eggs and fish, (particularly oily and/or long-lived species). Exposure is generally well characterised and quantified for PCBs and PCDD/Fs and a range of organochlorine pesticides. The vast majority of adult exposure will be below current WHO guideline values. Individuals exceeding the guideline value will be dominated by subsistence fishermen and their families, individuals who consume several meals of oily fish each week in addition to those consuming locally produced foods in the vicinity of an on-going source of contamination.

- Human lipid concentrations of well-characterised compounds such as PCBs and PCDD/Fs have been declining significantly in recent years throughout the Region at a rate of approximately 5% per year since the early 1990s. This decline coincides with European restrictions on the manufacture and release of these compounds into the environment and in particular, into the atmosphere. For some PTS compounds of emerging concern such as PBDEs, there is some evidence of increasing trends in human breast milk during the last 20 years.

- Breast-fed infants represent a distinct sub-group of the population whose exposure to PCDD/Fs and Dioxin-like PCBs will exceed current guideline values based on body-weight for the first few months of life. In view of the significant declining trends in TEQ concentrations in breast milk over the last 20 years, WHO strongly recommends that breast-feeding is encouraged and promoted for the benefit of the child.

4. ASSESSMENT OF MAJOR PATHWAYS OF CONTAMINANTS TRANSPORT

As many persistent toxic substances are semi-volatile, their atmospheric transport can occur either in the gas phase or in the particle phase of the atmosphere. Due to their low vapour pressure, PTSs tend to partition mainly into organic carbon containing media, such as soil, sediment, biota or aerosols. However, their volatility is often high enough to allow for long-range transport in a way that has been described as the "grasshopper effect". This means that the chemical is trapped in an organic phase without being degraded, and is then released back into the atmosphere, allowing for a short transport, after which it is trapped again and the procedure continues until the chemical is ultimately degraded. This "grasshopper effect" allows persistent chemicals of low vapour pressure to be transported long distances to areas where they have never been used, which is of concern both for ethical and environmental reasons. Transboundary movement may also be possible via large water bodies, where chemicals of low water solubility can be transported a long way via water particles and suspended sediment material or chemicals with high water solubility can be very effectively transported in the dissolved state. Migrating fish could also contribute to this phenomenon.

Regardless of which medium a chemical is being transported in, what ultimately determines a chemical's potential for long-range transport and thus transboundary move-

ment are its partitioning properties in combination with the nature of the environmental media in or between which the transport occurs. Therefore, crucial in order to achieve an adequate description of a chemical's movement is to create a picture, which accurately describes the possible transport pathways that a chemical substance can undergo. This is a complicated task, since the complexity of the environment cannot be underestimated. As a first approach, the environment can however be divided into basic units, or compartments, which might include air with aerosols, water with water particles, soil, sediment and vegetation, or other significant media. The aim is then to achieve a description of transport processes and to derive a full picture of the movement of chemicals within the region being assessed.

Today, most PTS are banned and not “primarily” emitted in the European region. Transboundary air transport has been shown to be important for the occurrence of these chemicals in Northern Europe. Atmospheric deposition is an important pathway for PTS to both aquatic and terrestrial ecosystems. The cold climate in the northern part of the region may favour the deposition of the PTSs. Environmental compartments, such as vegetation, soil and sediments, will act as reservoirs for PTSs. In this region, contaminated sites, so-called “hot spots”, will also constitute as significant reservoirs for PTSs. PTSs may be re-emitted back from the ecosystem to the atmosphere and be transported both within and from the region into the arctic areas (grasshopper effect).

Conclusions

- Transboundary transport is important for the occurrence of PTS in the European region. Atmospheric transport processes are important pathways for PTS to both aquatic and terrestrial ecosystems.
- The evidence of LTR in the region has been investigated both with measurements and modelling.
- An integrated monitoring/modelling approach is applied for assessment of PTS contamination in the European region. This approach includes arrangement of a superstation network, model assessment of contamination levels and national measurement campaigns. In modelling activities accumulation in the compartments other than atmosphere is important.
- At present there exist a lot of multi-compartment PTS transport models, both steady-state and dynamic, describing PTS' fate in the environment. In the framework of the LRTAP Convention the EMEP/MSCE-POP model is used for assessment of PTS contamination in the Region.
- Modelling activities are useful for evaluation of PTS redistribution between various environmental compartments, long-term trends of environmental contamination, spatial distribution of concentrations in different media (atmosphere, soil, seawater, vegetation) and transboundary transport.
- Some PTS possesses very high long-range transport potential and a hemispheric/global scale is reasonable then in order to assess their contamination in Europe. The hemi-

spheric version of the EMEP/MSCE-POP model indicates the ability of some PTSs to transport to and from the European Region.

- PTS often possesses very high long-range transport potential and a hemispheric/global scale is reasonable to assess European contamination. The results of the EMEP/MSCE-POP model indicate the ability of some PTS such as PCBs, PCDDs/Fs, g-HCH.

5. PRELIMINARY ASSESSMENT OF THE REGIONAL CAPACITY AND NEED TO MANAGE PTS

Region III has 29 countries, 22 of them signed and 8 already ratified the SC. Many countries of the Region also signed (24 from 36 which signed this Protocol in that time) and ratified (11 from 12) the Aarhus Protocol to the Convention on Long-Range Transboundary Air Pollution on POPs.

The production and use of PCBs and OCPs are restricted or banned with very few exceptions. Air, water, soils, plants and foods are legally protected against hazardous substances in the Region. The PTS inventories of releases to air, water, land and products are ongoing processes. Few countries have a complex emission inventory based on the measurement of real emission factors, all countries based on EMEP and CORINAIR activities are using the European Atmospheric Emission Guidebook for annual inventory, but lack of actual inventories exists as far as water and land releases and the products contents of PTS are concerned. The most “open” problem is PTS by-products such as PCDDs/Fs, PAHs and HCB. Also the inventory of obsolete pests is at the acceptable level. The evidence of PTS hot spots is still a problem in CEECs.

Conclusions

- The production and use of PCBs and OCPs are restricted or banned with very few exceptions. the Region has the legal, economic and political capacity for solution of PTS environmental problems, mainly because of the EU strategy and co-operation between EU and accession countries.

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MONITORING OF PERSISTENT ORGANOCHLORINE PESTICIDES IN SOILS OF THE CZECH REPUBLIC

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INTRODUCTION

Organochlorine pesticides are an important component of persistent organic pollutants in the environment. These substances are not characterised by high acute toxicity for hot-blooded animals but they are very stable and hard to biodegrade. In addition they are strongly lipophilic what means high risk of accumulation in the fat tissues.

OBJECTIVES

In the period 1994 – 1997 organochlorine pesticides' contents were observed on variable set of observation places in the Czech Republic. Since 2000 we have been observing DDT and its metabolites, HCHs and HCB on stable set of 40 localities of the "Basal Soil Monitoring".

The reason for regular monitoring is need to evaluation of contamination level and changes assessing in long-term scale and assessing of the risk for the environment and food chains. Created database may be used for risks assessing in extraordinary events (e. g. floods 2002 in the Czech Republic).

SAMPLING AND ANALYSIS

Area for composite sample represents 1000 square metres and is determined by geographic coordinates, morphology of terrain, climatic and soil parameters. One composite sample of topsoil consists of at least 30 punctures of boring bar.

Samples had been supplied to the chemical lab, dried, homogenized and stored at -18°C in glass bottles.

Target analytes were extracted into hexane / acetone mixture (3:1) by SOXTEC extractor [Tecator]. Two internal standards PCB30 and PCB155 were added and extract was cleaned up on SPE column with silikagel sorbent. Clean eluent was evaporated and redissolved in 2 ml of isooctane, transferred into vial and was ready for GC/MS analysis.

Chromatographic conditions:

Gas chromatograph GC 8000 with MD 800 [CE Instruments]

Capillary column DB XLB [J&W Scientific], 30m x 0,25 mm x 0,25 μm .

Injector temperature (split/splitless) 250°C

Detector temp. (source/interface) $200/250^{\circ}\text{C}$

Temperature programme $100/200/280^{\circ}\text{C}$

Rate $30/5^{\circ}\text{C}/\text{min}$

Time 1/1/10 min

SSL Time 10 sec, 1 μl , Helium flow 30 cm/sec

LOQ = 1 $\mu\text{g}/\text{kg}$ dried sample for DDT, DDE, DDD, HCH (0,5 $\mu\text{g}/\text{kg}$ for HCB)

LOQ = 0,5 $\mu\text{g}/\text{kg}$ dried sample for HCB

Note: Samples in years 1994-1997 were analysed on chromatograph with ECD.

Year	Number of samples	HCB		HCHs		DDT		DDE		DDD	
		median	min. - max.	median	min. - max.	median	min. - max.	Median	min. - max.	median	min. - max.
1994	41	5,00	<0,5-10,0	2,00	<0,5-14,0	7,00	<0,5-66,0	2,50	<0,5-34,0	<0,5	<0,5-13,0
1995	39	5,70	<0,5-12,5	<0,5	<0,5-7,7	7,90	<0,5-41,5	1,40	<0,5-21,0	0,60	<0,5-8,9
1996	28	6,10	<0,5-10,1	<0,5	<0,5-20,9	7,80	1-49,2	1,90	<0,5-29,8	0,90	<0,5-8,7
1997	35	7,10	1,2-24,0	1,00	<0,5-39,1	10,10	<0,5-739,0	5,15	<0,5-823,1	<0,5	<0,5-27,9
2000	40	1,80	<0,5-10,6	<1	<1-<1	26,00	<10-649,0	1,65	<1-387,7	<1	<1-40,0
2001	40	3,10	<0,5-19,0	<1	<1-<1	6,60	<1-420,8	3,65	<1-588,6	<1	<1-36,9
2002	40	5,45	0,7-34,0	<1	<1-3,7	3,80	<1-293,7	3,20	<1-141,6	<1	<1-48,5

Table 1:

Data about contamination of topsoil of agricultural land by HCB, HCHs, DDT and its metabolites in the Czech Republic ($\mu\text{g}/\text{kg}$ -1 of dry soil matter)

RESULTS OF BASAL MONITORING

These results are shown in Table 1, current national limits in the Czech Republic defined by ordinance No. 13/1994 and limit values by proposal of upgrade of this ordinance in Table 2.

The medians of HCHs' contents are very low, mostly around detection limit and always under our national limit. Current limit value of HCB is 10 ug.kg⁻¹ of dry matter and we found values mostly in interval 1 – 20ug.kg⁻¹. Only in 1994 there was no sample above national limit, in the other years there were some samples that exceeded this value. But if we use the limit value from proposal of upgrade of current ordinance that should be 20 ug.kg⁻¹ of dry matter, this limit will not be exceeded in samples of 5 years.

In case of DDT and its metabolites the medians mostly don't exceed our limit value but some extreme values exceed it several times. These extreme values are usually caused by old loads, most often on soils with intensive long term growing of vegetables, potatoes, optionally horticulture plants. On these areas were persistent organochlorine pesticides used in big amounts in past. We can't also leave out the impact of long transboundary transport of POPs.

FLOODS IN 2002

Catastrophic floods in 2002 affected enormous area of agricultural land and were discussed from view of

	HCB	HCHs	DDT	DDE	DDD
Ordinance No. 13/1994 Sb.	10	10	10	10	10
Proposal	20	10	30	25	20

Table 2:

Limit values of Persistent Organochlorine Pesticides in soil by ordinance No. 13/1994 Sb. and by proposal of a new ordinance (ug.kg⁻¹ of dry soil matter)

possible contamination of flooded soil by hazardous elements or substances from industrial companies, stocks or urban areas which were washed out during floods.

Analyses of soils samples from flooded areas (Table 3) have mostly shown lower levels of HCB and HCHs than permissible values of pollution. Content of DDT and its metabolites have exceeded permissible values approximately in half of samples but some extreme values were found too. Since contents in sediments, which were sampled on affected soils, were often strongly lower than contents in soils we could have said that floods did not cause these high values. In the case of the biggest measured value (DDT more than 2000 ug.kg⁻¹ of dry matter) there was made out that on this plot was an illegal waste site in past.

District	Number	Crop	HCB	HCHs	DDT	DDE	DDD
Litoměřice	1	arable land	1,4	2,0	14,3	23,8	4,2
	2	arable land	0,6	2,0	1,3	4,1	<1,0
	3	arable land	2,4	2,0	171,5	149,8	12,2
	4	arable land	4,9	2,0	289,5	244,3	23,3
	5	arable land	1,1	2,0	143,2	244,6	10,6
	6	arable land	7,4	2,0	155,3	140,6	17,0
	7	arable land	1,3	2,0	9,7	20,1	2,3
	8	arable land	1,8	9,4	30,1	54,2	1,7
	9	arable land	3,8	11,0	48,0	105,2	4,8
	10	arable land	3,5	14,2	216,4	248,7	7,3
	11	arable land	<0,5	2,0	7,6	12,5	1,5
	12	arable land	<0,5	2,0	1,4	3,7	<1,0
	13	arable land	6,2	2,0	36,8	61,4	2,5
	14	arable land	5,8	2,0	24,8	28,0	1,4
	15	arable land	1,3	2,0	11,2	14,1	7,4
	16	sediment	1,0	2,0	<1,0	2,9	1,4
Ústí nad Labem	17	meadow	10,1	2,0	203,7	104,9	21,1
	18	gardens	3,6	6,2	202,1	95,7	25,6

Table 3:

Values measured on localities affected by flood (ug.kg⁻¹ of dry soil matter)

District	Number	Crop	HCB	HCHs	DDT	DDE	DDD
Plzeň-city	19	arable land	10,1	20,9	2069,2	554,0	127,6
	20	sediment	5,5	20,7	60,1	39,0	23,1
	21	arable land	13,9	6,3	539,8	173,2	32,1
	22	sediment	6,2	10,3	27,0	38,1	27,1
	23	meadow	2,7	5,0	17,9	15,3	7,7
Plzeň-north	24	arable land	6,5	8,5	319,9	93,9	315,5
Rokycany	25	arable land	2,7	2,0	11,3	8,3	1,8
Mělník	26	forest nursery	44,3	59,6	204,1	74,6	23,5
	27	arable land	3,7	2,0	10,1	10,6	3,0
Praha-west	28	arable land	5,5	2,0	110,4	158,2	8,9
Znojmo	29	arable land	2,3	2,0	252,5	223,4	6,5
	30	arable land	2,1	2,0	26,0	40,2	1,4
Jindřichův Hradec	31	arable land	2,7	5,9	142,7	90,1	60,5
	32	arable land	3,1	2,0	14,5	8,2	1,8
Strakonice	33	gardens	1,3	3,7	32,4	7,2	5,2

RESULTS

Elaboration of the database of persistent organochlorine pesticides' content in soils allowed us following changes of these risk substances in long-term scale.

Long termed observation provides comparative values for assessing of possible pollution in some extraordinary events (e. g. floods, industrial accidents etc.) and gives grounds for participation on discussions

about hygienic limits of these substances in the environment.

After floods in 2002 we could exclude influence of this event to soils contamination. The most probable source of high concentrations that were found is previous long-term use of persistent organochlorines by growing vegetables, potatoes etc. We have to take into account effect of long transboundary transport too.

PROTECTION, TRIGGER AND CRITICAL VALUES FOR PERSISTENT ORGANIC POLLUTANTS IN SOILS OF BULGARIA

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ABSTRACT

In the year 2000, the Ministry of the Environment and Waters in Bulgaria published an annex to the Ordinance No

3 (1979) where the precaution, trigger and critical values for soils have been involved for 16 PAHs, 6 PCBs and 6 chlorinated pesticides. For PAHs and PCBs, the precaution values have been set on the basis of their naturally occurring background concentrations in the soils. The trigger and critical values have been derived on the basis of effect-based approach, using (eco) toxicological data about trigger concentrations (MPC) and negligible concentrations (NC). In the case of the absence of (eco) toxicological information, the final decision about values has been made by expert judgment

Concerning the chlorinated pesticides, the limits have been derived using data of long-term (eco) toxicological experiments and risk analysis. The precaution as well as maximum acceptable and critical values are designed as numerical limits, equal to all soils with organic content < 5,0 %. The evaluation of soils polluted by POPs depends on their concentration levels in the upper (0-20 cm) soil layer, expressed as total amount in mg/kg dry soil. For analysis, the extraction procedure according E DIN ISO 10382.02.98 and E DIN ISO 13877:06.95 with modification for pesticides is recommended.

The values have been adopted as “official” critical limits in order to be used as a tool for the assessment of the degree of *in situ* pollution with persistent organic chemicals, setting priorities in control measures and deriving emission reduction goals.

INTRODUCTION

The first standards for polluted soils have been established in Bulgaria in 1979. These standards included limited number of inorganic contaminants. Until recently, the organic pollutants in the soils have not been the focus of the investigations and standards for these pollutants have been adopted only in the year 2000.

The investigations of the Persistent Organic Pollutants (POPs) in the soils of the country began after 1990 and are related only to the restricted areas around the point or liner saucers. The results obtained by *Atanassov et al. (2000)* showed, that Polycyclic Aromatic Hydrocarbons (PAHs) content of 150 soil samples vary between 0,069 (50 p values) and 0,145 mg.kg⁻¹ (90 p values). For individual compounds, the PAHs with 2- 4 aromatic rings prevailed, such as naphthalene, phenanthrene and fluoranthene. PAHs with 5-7 aromatic rings, exhibited very low concentrations in soils, which vary between 0,001 and 0,005 mg.kg⁻¹ dry soil (*Atanassov et al. 2002*). They also found that concentrations of benzo (a) pirenene in the soil samples vary between 0,002 and 0,005 mg.kg⁻¹ dry soil which are comparable with background concentrations (*Shegunova et al. 2002*).

The content of Polychlorinated Biphenyls (PCBs) and Lindane (HCH) in soils is negligible and varied according to the detection limits of these compounds.

More data can be derived about the content of organochlorine pesticides in the soils. Until now most agricultural soils contain traces of DDT and its metabolites. Some soils surrounding the pesticides warehouses of former cooperative farms in Bulgaria contain higher levels of p,p'-DDE, p,p'-DDT and o,p'-DDT (*Balinova, 1998*).

As a whole, no urban land or agricultural soil polluted with PAH and PCB have been registered officially (*Todorova, 2002*). But in agreement with the European Standards, the Ministry of Environment and Waters (MEW) of Bulgaria identified during 1997 what is called “Priority pollutants”. These pollutants included 16 PAHs, 6 PCB and some of the persistent chlorinated organic compounds, which are used as pesticides and are included in the DDX group. All these compounds represent important contaminants because of their widespread distribution in the environment and their toxic properties. Most of them are quite resistant to degradation and tend to be accumulated in soils, plants, waters and other components of the environment.

Taking into account the potential risk from the accumulation and the hazardous effect of the organic pollutants in soils, the Ministry of Environment and Waters of Bulgaria started in 1999 a special project for deriving generic soil values for POPs. The main objectives and results of this project will be presented and discussed in the present paper.

MATERIALS AND METHODS

The project involves derivation of three generic standard values for POPs in soils, namely: precaution, trigger and critical values relating to 16 PAH, 6 PCB and 6 chlorinated pesticides (Table 1). The precaution values are defined as the concentration of POPs in the unpolluted and multifunctional soil. These values cover the precautionary protection of sensitive soil functions in and can serve as standards for good and healthy soils.

The trigger values are established as uniform screening concentrations indicating some pollution levels of this soil that needs further investigation to be confirmed (or otherwise) indicating that potentially dangerous concentrations of hazardous substances exist.

The critical (or “intervention”) values are designed as uniform predetermined soil quality standards indicating the existence of hazardous concentrations of the POPs in the soils, which need immediate elimination without any further investigation.

As the concepts for the precaution, trigger and critical concentrations of pollutants in the soil were stressed by *Ferguson, 1999*, it seems now to be generally accepted, especially in CARACAS countries. Most of the European countries use these concepts to set up generic soil quality values as a tool for implementation of soil policy protection. The same is the case of Bulgaria with the levels of POPs in soils.

The protection system using the precaution, trigger and critical levels has been applied earlier in Bulgaria for evaluating the soil pollution by heavy metals, oil products and radionuclides (*Atanassov et al., 1993, MAF, 1994*). Now this system is extrapolated to POPs in the soils and embraces practically all-important organic contaminants.

Three main criteria have been used for setting up precautionary, trigger and critical values. These criteria are background levels in soils, maximum acceptable risk levels (MAR) of organic pollutants in soils and the comparison of these values with the accepted numerical values used in other countries.

The precaution values have been set up using the background reference values for PAH and PCB in the soils of Bulgaria. These concentrations have been obtained on the analytical basis of 106 soil samples, taken from the upper (0-20 cm) layers of nine wide spread Bulgarian soils as 90 p concentration calculated, according to the method of *Labo, 1995*

The background values for PAHs and PCBs are published in the works of *Atanassov et al. 1999 and 2002 and Shegunova et al., 2002*. As a rule, the proposed precaution values prevail the reference background values for individual compounds of PAHs and PCBs between 2-10 times (Table 1), depending on the potential toxicity of the individual compounds.

To derive precaution values for PAHs and PCBs, the maximum acceptable risk levels (MAR) have been used by *van de Meent et al., 1999 and Tertytze, 2002*.

Both trigger and critical values are risk based. The maximum acceptable values have been obtained using the rec-

ommended MAR or NOEC values for PAHs, PCBs and safety factor = 10. The safety factor showed the interactive effect of substances, the difference between acute and chronic effects and the differences between measurements made in the laboratory and those made in the field (Terytze, 2002).

The critical values have been defined on the basis of MAR levels without using safety factor. The objective in this case is to protect the exposed population or components of the environment from all hazardous effects where exposure never exceeds the ecotoxicological or toxicological reference values (Bissonnet, 1998).

The third criterion used for setting the protection, maximum trigger and critical values, was the comparison of the Bulgarian values obtained with those adopted in other countries. This approach is recommended by Hammann and Gupta, 1998. A review of limiting values for POPs in soils adopted in some countries is published in the work of Visser, 1993.

Soil values for POPs, presented in Table 1 have been derived for individual substances as well as for the sum of PAHs, PCBs and chlorinated pesticides.

The values have been designed as rigid numerical values equal for all types of soils and are not depending on its texture, soil reaction (pH) or land use activity.

These values represent the total amount of these pollutants in the upper (0-20 cm) soil layer and cover all soils with humus content < 5.0 %. On the other hand, soils with humus content > 5.0 % in Bulgaria occupy only 3.4 % of the total territory of the country and can be excluded without a risk from the implementation of the soil protection policy (Atanassov, 1999).

DISCUSSION

In Bulgaria, until now there is no special law for contaminated lands. A key policy document is Ordinance _ 3, dated 1979 and complemented few times later which is a part of very general Law of Environmental Protection. The development of soil quality standards is going without a suitable framework for regulating and providing guidance on contaminated sites. There are no established national methodologies or criteria for assessment and remediation the polluted sites. Therefore, setting national soil quality standards require necessarily comparing between these standards with the standards adopted in the countries with more advanced legislation in the area of soil protection.

The numerical limits shown in Table 1 for PAHs, PCBs and chlorinated pesticides in soils are comparable with the values adopted in some other countries like Netherlands and Germany (Visser, 1993). So far, the values in Table 1 are generic for all land use activities. The values defined for the sum of PAHs was found to be higher than the values proposed for sensitive land uses, fixed in Berlin list part 2. But trigger values for the individual substances are on the frame of the limits, accepted in CARACAS countries. Thus, the generic numerical limits for PAHs, PCBs and chlorinated pesticides can be used as

a tool for soil protection as well as an instrument for setting remediation objectives. Based on the values in Table 1, three possible concentration zones can be defined for each contaminant as well as an instrument for setting remediation objectives. In the first zone, the contaminant is below the trigger values and its concentration is comparable with background (where exist) or precautionary values. The soil can be considered as non polluted and multifunctional, and can be used without risk for the environment as well as for the public health. Concentrations that are between maximum acceptable and critical levels will indicate pollution problem but do not automatically imply that significant risk due to contamination exists. This will require the competent authority to provide an investigation to establish the extent of contamination: low, middle or high according to the prevailing concentration [Low= two, Middle= three and High= fivefold the trigger concentration]. Finally, the third zone containing levels of the contaminant above the critical values where the concentration is high enough to induce a significant risk and therefore, the soil can be defined as highly or significantly polluted.

In Bulgaria there is no national standards for the analyses PAHs and PCBs in soils. It was stressed by Terytze, 2002 that there is no consensus about the suitable methods for determining the available fractions of organic pollutants in soil. Thus, in the case of Bulgarian limit values for POPs it is recommended that total concentrations of these pollutants to be analyzed using standardized ISO methods.

Among these methods ISO 1387:1998; ISO/DIS 10381-2 and ISO/DIN 11464 can be mentioned to correlate the sampling, sample treatment, extraction and analysis of individual PAH, PCB and chlorinated pesticides. Selection of ISO methods is important for harmonization of the procedures and obtaining data which will be comparable with other European countries.

CONCLUSION

This paper describes a system for the assessment of the degree of Bulgarian soil pollution with PAHs, PCBs and chlorinated pesticides according to three limiting values namely precaution, trigger and critical. The limiting values are designed as generic numerical values for all soils of Bulgaria with organic matter content in the upper soil layer < 5.0 % regardless the texture, reaction and land use type of the soil. The results obtained are comparable with the limit values for POPs adopted in some European Countries and are compatible with the ISO-190 recommended analytical methods. Based on the numerical values proposed, it is possible to assess the contamination of the Bulgarian soils with POPs more realistically. It is supposed that further activities shall be focused on the development of more differentiated limit values for POPs in soils according to land use type. It is necessary to a more complete and advanced national legislation on soil protection to be established together with criteria for regulating and providing guidance on contaminated sites.

N ^o	Pollutants	RF	P	MA	C
I. Polycyclic Aromatic Hydrocarbons (PAHs)					
1	PAN ₁₆ (summa)	0,150	0,40	2,0	10
2	Naphthalene/NAP	0,022	0,04	0,1	–
3	Acenaphthene/ACE*	0,010	0,03	0,2	–
4	Acenaphthylene/ACY*	0,003	0,03	0,2	–
5	Fluorene/FLU*	0,010	0,03	0,3	–
6	PhenanthrenePHE	0,015	0,045	0,4	–
7	Anthracene/ANT	0,005	0,050	0,5	–
8	Fluoranthene/FLA	0,015	0,020	0,1	–
9	Pyrene/PYR*	0,008	0,020	0,2	–
10	Benzo[a]anthracene/BaA	0,003	0,020	0,2	–
11	Chrysene/CHR	0,008	0,020	0,2	–
12	Benzo[b]fluoranthene/BbF + Benzo[j]fluoranthene/BjF + Benzo[k]fluoranthene/BkF	0,016	0,020	0,2	–
13	Benzo[a]pyrene/B _a P	0,005	0,015	0,1	–
14	Benzo[e]pyrene/BeP**	0,008	0,020	0,15	–
15	Indeno[1,2,3-cd]pyrene/IND	0,011	0,020	0,2	–
16	Dibenz[ah]anthracene/DbahA*	0,002	0,020	0,1	–
17	Benzo[ghi]perylene/BghiP	0,004	0,020	0,1	–
II. Polychlorinated Biphenyls (PCBs)					
18	PAN ₆ (summa)	0,005	0,02	0,2	1
19	2,4,4'-trichlorobiphenyl PCB-28	0,001	0,001	0,01	
20	2,2,5,5'-tetrachlorobiphenyl PCB-52	0,001	0,001	0,01	–
21	2,2,4,5,5'-pentachlorobiphenyl PCB-101	0,001	0,004	0,01	–
22	2,2',3,4,4',5'-hexachlorobiphenyl PCB-138	0,001	0,004	0,04	–
23	2,2',3,4,4',5,5',-hexachlorobiphenyl PCB-153	0,001	0,004	0,04	–
24	2,2',3,4,4',5,5',-heptachlorobiphenyl PCB-180	0,000	0,004	0,04	–
III. Chlorinated pesticides					
25	Hexachlorobenzene	–	0,025	0,25	5
26	α-β-γ-Hexachlorocyclohexane	–	0,001	0,01	2
27	Dichlorodiphenylkalogenoethane/DDX(summa__ DDT, DDD _ DDE	–	0,3	1,5	4
28	2,4' and 4,4'- Dichlorodiphenildicloroethylene /-o,p'-and p,p'-DDE	–	0,1	0,5	–
29	2,4' and 4,4'-Dichlorodiphenil-2,2-di- chloroethane/o,p'-and p,p'-DDD	–	0,1	0,5	–
30	2,4' and 4,4'-Dichlorodiphenil-2,2,2-tri- chloroethane/o,p' and p,p'-DDT	–	0,1	0,5	–

* - expert values

** - as to Benzo[a]pyrene

Table 1.

Reference Background (RF), Precaution (P2) Maximum Acceptable (MA3) and Critical (C4) Values (mg/kg dry soil) of POPs Bulgarian soil

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EVALUATION OF LIMING OF A HEAVILY HCH-CONTAMINATED SOIL IN RIO DE JANEIRO

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INTRODUCTION

Industrial sites where lindane was produced or stocked need remediation nowadays given its persistence in the environment. This is a pioneer study on liming of contaminated soils and its effects on soil microbiota and chlorinated compounds under tropical conditions. Lindane was produced in the Rio de Janeiro metropolitan area between 1950 and 1955 and HCH isomers were discarded in the open, outside the factory. When the plant was

closed down, large amounts of HCH were left behind. Part of the product was spilled and entered the environment in the following years when the buildings were demolished. In the late eighties HCH was being sold in the local markets as medicine against lice, which led the authorities to decide for a cheap remediation of the area: liming. Calcium oxide and water were roughly mixed to the HCH-contaminated soil with a tractor, to promote the dechlorination of HCH. Consequently the polluted surface was increased and great heterogeneity was introduced in the soil (Borges, 1996). Before any new treatment could begin at the polluted site, an assessment regarding soil microbiota, contaminants and the overall process after liming was necessary. The purposes of this study were to (1) evaluate the efficiency of the liming process, (2) assess the impact of HCH and liming on the microbiota of contaminated and non-contaminated soil and (3) supply chemical and microbiological data on the soil after lime addition.

The contaminated site is located within the floodplain area of the Iguaçu River, which runs southeast from the Serra do Mar Massive (1,000 m above sea level, in average) towards Guanabara Bay. Climate is typically hot and wet. Geological-geotechnical investigations showed the presence of Quaternary sedimentary soil profiles 20 to 25 m deep, with fine to coarse-grained sediment mixtures or interbedded layers of clayey and sandy sediments, with a complex, laterally discontinuous distribution pattern (Barreto, 1998). Under this sediment, residual soil of unknown thickness occurs, the basement rock being mostly of gneissic origin. Table 1 shows some physical-chemical properties of superficial materials from the main contamination site, and of samples from uncontaminated spots. The material used in this investigation is representative of a profile having a clayey soil on top of a sandy one. Soil mineralogy data indicate a low physical-chemical reactivity of the material at the site.

Property		Material				
		A ⁽¹⁾	B ⁽²⁾	C ⁽³⁾	D ⁽⁴⁾	E ⁽⁵⁾
Grain size distribution (% in weight)	Medium to Coarse	25 to 54	36	22	20	54
	Fine Sand	14 to 46	14	12	33	14
	Silt	5 to 32	6	8	37	24
	Clay	3 to 44	44	58	9	8
Organic Matter (% in weight)		–	0,63	0,24	1,81	0,77
PH		acid*	4,8	4,6	4,8	8,8
Soil Chemistry	Al ³⁺ (meq/100ml)	–	1,4	12,2	1,2	0
	Ca ⁺⁺ (meq/100ml)	–	0,4	0,9	1,2	3,8
	Mg ⁺⁺ (meq/100ml)	–			1,2	11,3
	Na ⁺ (ppm)	–	60	50	28	18
	K ⁺ (ppm)	–	70	20	125	39
	H ⁺ (meq/100ml)	–	2,9	19,0	4,4	0
	P (ppm)	–	–	–	2	1
Cation Exchange Capacity (meq/100ml)			4,8	32,2	9,3	15,2

Table 1: Physical-chemical properties of the superficial soil at the area

(1) Soil down to 0,80m depth, retrieved from four trenches opened inside the main contamination area, before lime addition (Barreto, 1998).

(2) Uncontaminated fill soil retrieved from circa 0,20m of depth, some 300m from the main contamination focus (Borges, 1996).

(3) Uncontaminated clayey soil retrieved from circa 0,50m of depth, some 300m from the main contamination focus (Borges, 1996).

(4) Uncontaminated silty-sand soil retrieved from circa 0,30m depth, some 1.500m from the contaminated area. This material was used in the main microbiological essays.

(5) Sandy soil from the contaminated area (~ 0,30m), retrieved after lime addition, near trench 4. This material was used in the microbiological essays.

* Oliveira, 1994

MATERIAL AND METHODS

Evaluation of HCH distribution Contaminated soil was obtained in the centre of the pollution focus. Non-contaminated soil was collected in the same area, 1,5 km from the epicentre of contamination. Despite HCH's documented biodegradability, climatic conditions in Rio de Janeiro demanded a preliminary study of its degradation. A study in simulated conditions meant to determine the fate of HCH after liming and whether the site had been successfully remediated; reactions may stop in intermediate compounds and not lead to the mineralisation of the pollutant (Reineke, 1984). Only aerobic degradation processes were evaluated in this study as liming involved great revolving of soil superficial layers.

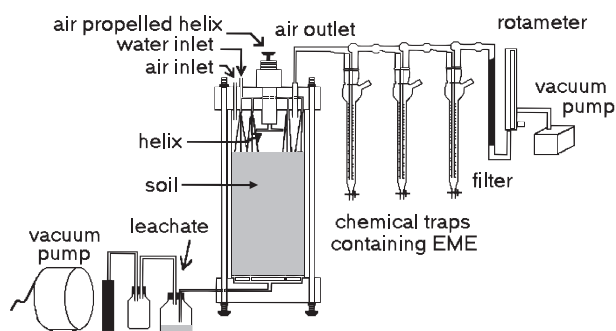


Figure 1: Microcosm system

Field conditions were simulated in microcosms where airflow (wind), water supply (rain), temperature and soils used were controlled (Figure 1). Soil columns were placed in stainless steel cylinders; leachate was collected under vacuum, simulating soil suction, and volatilisation products were caught in chemical traps containing ethylene glycol monomethyl ether (EME). Water content in the soil varied during the experiments according to water addition, percolation and volatilisation, as occurs in natural environments. (Schroll et al. 1994).

To evaluate field conditions, structured soil columns were collected in the contaminated area 15 months after liming, and volatilisation samples were collected in the laboratory. Composite soil samples from the contaminated area were also analysed.

Non-contaminated soil was mixed to HCH and to HCH and lime to study HCH distribution and degradation. Soil density in the microcosms was 1,2 g.cm⁻³ and pH went from 5 to 9 after HCH and lime addition. HCH used in simulation assays was collected from the heap of HCH left at the location of the former plant. Microcosms were kept at room temperature (19oC/22oC), water was added twice a week for 30 days. Soil, leachate and EME samples were hexane-extracted, extracts analysed by gas chromatography (Varian model 3600 CX and Shimadzu CG-14 gas chromatographers, equipped with electron capture detectors).

Studies of microbiota Composite soil samples of contaminated and non-contaminated soil were collected to a depth of 12 cm. Colony Forming Units (CFU) counts determined total culturable heterotrophic bacterial population (Lorch et al., 1995). Strains selected by their colonial and cellular morphology were isolated for identification (API-NE kits, Biolab-Mérieux, for Gram-negative bacilli; catalase, oxydase, endospore formation tests and specific growth conditions for Gram-positive strains - Holt et al., 1994).

Soil respiration determined the effect of contamination and liming. Uncontaminated soil was mixed to 40 mg HCH /g soil and to 40 mg HCH /g soil plus 40 mg/g lime. CO₂ evolution was measured for four weeks (Zibilske, 1994) and microbial response to higher oxygenation was ascertained by introducing O₂ in soils.

Respiration of composite samples of field contaminated soil and uncontaminated controls were compared for ten weeks, with aeration of the samples and nutrients addition (1:10 Simple Broth medium). Because of lime-induced pH shift, CO₂ may be transformed to bicarbonate, thus remaining trapped in soil and not being caught in the chemical traps. Bicarbonate amounts were determined in soils in all soils after one week (EMBRAPA, 1979).

The survival capacity of the culturable bacterial population of non-contaminated soil was evaluated with different amounts of HCH. Soil samples were mixed to HCH, incubated at room temperature and CFU counts were evaluated for 30 days.

RESULTS AND DISCUSSION

Calcium oxide increases soil polarity, enhancing partition of HCH towards non-polar soluble organic matter, and promotes a higher aggregation of soluble organic matter, reducing its mobility in soil and increasing soil porosity (Romkens & Dolfing, 1998). This situation may explain more water percolating from lime-treated microcosms (Table 2) and, besides lime-promoted dechlorination and microbial degradation (Deo et al., 1994), less leaching of HCH per ml water observed in treated microcosms (Table 3). Despite no conclusive differences in total HCH amounts leached, HCH amounts per ml of percolated water are almost three times lower in lime-treated microcosms, while water flow is only twice as important. In non-treated soils, HCH molecules may leach more easily with soil colloidal particles, while leaching of HCH adsorbed to organic matter may be prevented in limed soils.

Microcosms	M1	M2	M3	M4
Injected	3240 ml in 30 days (756 ml/week)			
Leachate (ml)	759	902	1526	1369
water flow (ml/week)	177.1	210.5	356.1	319.4

Table 2: Water injected and percolated, water flow from all microcosms after 30 days.

However, in spite of this and its low solubility, microcosms bottom layers presented up to three times more HCH than superficial ones (Figure 2). Still, amounts in leachate are smaller than in soil, suggesting that even though HCH is vertically co-transported (Worrall et al., 1999), it is retained by the soil matrix, leading to its accumulation at the bottom of microcosms while preventing it from leaching. In addition, in non-treated microcosms, less stressed and more active microbiota and more available dissolved organic matter could lead to a higher mobilisation of dissolved organic carbon and more leaching of HCH (Gödde et al., 1996). Our results showed greater amounts of HCH in leachate than in volatilised products, despite lindane's high volatilisation rate. HCH volatilisation was enhanced in lime-treated microcosms (Table 3). Pesticides with low leaching potential tend to be less mobile in low humidity conditions because of stronger aggregation and incorporation into the soil matrix. The high rainfall conditions of this study probably intensified HCH leaching. However, our results show that volatilisation of HCH still is occurring in the contaminated area in Rio de Janeiro. Increased soil porosity could also allow free HCH molecules to volatilise more easily from superficial soil layers in lime-treated soils. HCH volatilisation could also be enhanced by co-distillation, HCH molecules being carried by the airflow with more volatile metabolites. Lime action has apparently antagonistic effects on HCH movement that should be further investigated (Taylor & Spencer, 1990; Waliszewski, 1993). Small quantities of HCH volatilised and leached when compared to amounts in soil, as formerly observed (Feidieker et al., 1995). No conclusions were possible about HCH trapped in non-treated and in lime-treated soils, but results showed that, 15 months after liming, the soil was not remediated. All isomers were found in samples from the contaminated area.

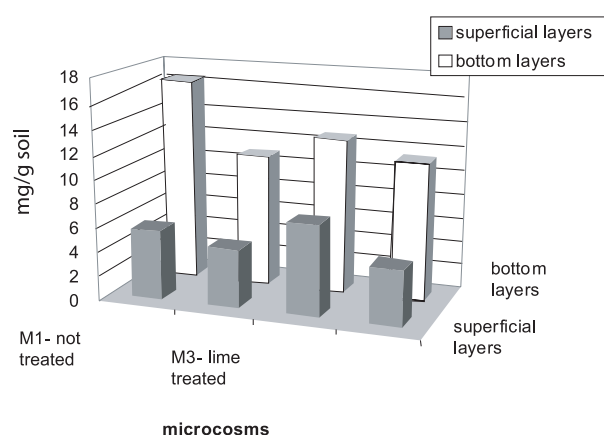


Figure 2: HCH in soil from superficial and lower microcosms layers (GC).

Microcosms		M1	M2	M3	M4
leachate (ug)	total HCH after 30 days	4944	1198.4	4167.2	5506.4
	HCH/ml water leached	9.167	11.31	3.197	4.150
volatilised (ug)	total HCH	45.75	63.60	132.4	976.4
soil (mg)	HCH/microcosm	49664	53645	52572	62450
	HCH/g soil	10.24	11.79	10.11	12.49
% HCH recovered		25.60	30.17	27.34	34.47

Table 3: HCH recovery: amounts in leachate, volatilisation and soil samples from the 30-day simulation assays (GC).

Chromatograms showed the appearance of new peaks, maybe from dechlorination metabolites, in samples from lime treated microcosms. Qualitative mass spectrometry analyses of one lime-treated microcosm detected chlorobenzenes and chlorophenols in all samples; dioxins were also found in field contaminated soil samples. Bastos (1999) and Braga et al. (2002) also detected dioxins as well as DDT and its metabolites in the same area. The emergence of still unidentified metabolites, makes risk assessment of the contaminated area much more difficult.

The lack of bacterial strains in one soil sample from the contaminated area (January 1998) was confirmed by a DNA extraction analysis; this may be explained by the unseasonable dry and hot climatic conditions during that summer, caused by a particularly strong manifestation of the El Niño South Oscillation phenomenon (INMET, 1998). Except for that sample, no great variation of soil culturable bacterial counts was observed over 14 months (Table 5). The high bacterial counts in field contaminated soil indicate the presence of a selected population adapted to HCH and lime amounts in soil and to alkaline pH. Probably because of this adaptation, bacterial strains presented poor survival capacity under laboratory conditions as well as a low morphological diversity in culturable populations. Some isolates were identified (Table 6), most of them being frequently found in soils and some known for their capacity of degrading xenobiotics other than HCH (e.g. Assaf & Turco, 1994; Sahu et al., 1990, 1995; Otte et al., 1993). Our study under tropical conditions showed the same pattern observed in other climates and bacterial capacity of degrading HCH and surviving in highly contaminated environments (e.g. Deo et al., 1994; Tu, 1976). However, lime-induced organic matter flocculation may imply in a lower availability of soil organic carbon and contaminants to microbiota, and lead to slower biodegradation. Conventional microbiology is limited because of the non-culturability of most environmental microbial strains; however, it can be a useful tool to rapidly and cost-effectively assess responses of microbiota to contamination, liming and stimulation.

volatilised in 7 days from undisturbed soil (mg)	HCH in composite samples of contaminated soil (mg/g)
57.75	13.89

Table 4: HCH in contaminated soil: total volatilisation after seven days (average of 4 microcosms) and amounts in soil field samples (average of 3 composite samples) (GC).

Date	Jan/97	Mar/97	Feb/98	Mar/98
Non-contaminated soils	1010	109	5.109	3.1010
Contaminated soils	3.107	109	n.d. a	4.109

a- n.d.: non detected

Table 5: Culturable bacterial counts in contaminated and non-contaminated soils (CFU/g soil). Means of 5 samples.

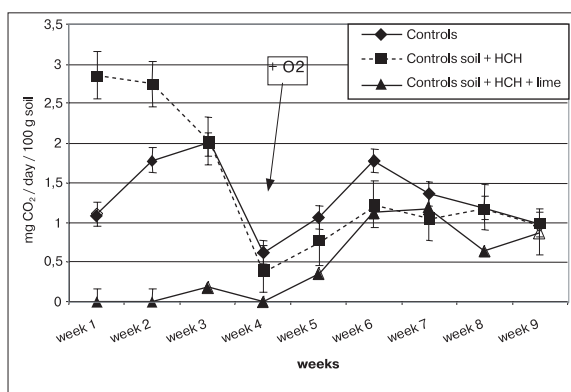


Figure 3: Respiratory activity in field non-contaminated soil (®) and contaminated soils (⌒) (mg CO₂/day/100g soil). Values are means of three samples.

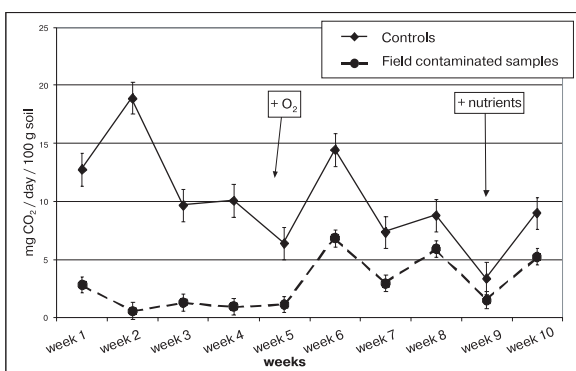


Figure 4: Respiration in simulation conditions: control soil (®), control soil + HCH (⌒), and control soil + HCH + lime (⌒) (mg CO₂/day/100g soil). Values are means of three samples.

Respiratory activity of contaminated field samples was lower than in non-contaminated soil (Figure 3). Addition of HCH stimulated respiratory activity at first, while it was almost eliminated by the addition of 4% lime; however, respiration was gradually resumed (Figure 4) showing the recovery capacity of microbiota. Carbonate and bicarbonate found in limed soils after 7 days (8.283.10⁻² and 7.414.10⁻⁴ mg/g soil respectively) confirm that CO₂ production was not suppressed by the pH shift, but it appears to be nonetheless inhibited to a certain degree. All samples responded to oxygen and/or nutrient addition, as previously observed by Tu (1975). Those are commonly used techniques for in situ remediation of soil and groundwater, which might be considered by local regulatory agencies for the area. Results also showed an increase in respiration with HCH addition to non-contaminated soils, confirming its lack of toxicity as well as a possible capacity of the

indigenous microbiota to use it as carbon source. As expected, high pollutant concentrations did not prevent bacterial growth. The 30-day experiment showed an important survival rate even in high amounts of HCH.

Table 6: Strains isolated from the contaminated site soil samples

	species	Isolated strains
	Acinetobacter lwoffii	1
	Burkholderia cepacia	3
GRAM	Chromobacterium violaceum	1
NEGATIVE	Comamonas testosteroni	1
	Pseudomonas chlororaphis	1
	Pseudomonas stutzeri	1
	Stenotrophomonas maltophilia	1
GRAM	Kurthia sp.	1
POSITIVE	Micrococcus halobius	1
	Micrococcus sp.	1

CONCLUSIONS

In this area in Rio de Janeiro, liming did not appear as an effective solution to degrade HCH, as it may have reduced pollutant availability to soil microbiota, and released more soluble, volatile and hazardous compounds, worsening air and groundwater contamination. Although liming probably slightly reduced total HCH amounts, mostly HCH still remains in soil, and degradation was not complete, while other liming-related problems emerged. This study may avoid future indiscriminate use of liming to remediate pesticides-contaminated areas. Future studies

may identify the optimal conditions to use the indigenous population combined to other remediation techniques to clean up the soil in the most effective manner.

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MONITORING WATER POLLUTING PESTICIDES IN HUNGARY

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ABSTRACT

Pesticides have been monitored in Hungarian surface waters including streams, rivers and lakes during a three-year period. In total, 354 samples have been collected between 2000 and 2002. Samples were collected annually in two runs: before and after spring and early summer pesticide applications. Target pesticide compounds included the presently registered and utilized active ingredients that potentially contaminate surface waters due to their physico-chemical properties or their mode of action. One or more pesticide active ingredients above the detection limit of the instrumental or immuno-analytical method used have been detected in 209 samples, giving the result that 59% of the samples collected throughout the sampling campaign contained pesticides residues.

INTRODUCTION

Surface waters are being contaminated with pesticide residues, regardless the economical development, in certain countries. A special problem is the presence of the persistent pesticides. Although the usage of persistent organic pollutants (POPs) is prohibited in many countries, pesticides that persist in soil throughout and among entire vegetation periods are still in use. Thus, pesticides residue analysis in environmental samples has received increasing attention in the last few decades resulting in many environmental monitoring programs for a broad range of pesticides.

A significant proportion of pesticides applied to cultivated plants do not reach their target site due to drifting, leaching and other off-target effects. Drift-off effects of volatile pesticides, leaching of soil disinfectants, run-off effects of persistent pesticides with natural precipitation pose a continuous risk to the quality of our natural water supplies. This calls urgent attention to two areas: (a) re-evaluation of environmental persistence and risks of the presently registered and applied pesticides, and (b) thorough monitoring of potentially water contaminating pesticides in surface water and in natural water bodies. Acknowledging these pressing needs, a nation-wide survey was carried out during the last three years in Hungary to identify local and non-point pesticide contamination sites in surface waters and raw drinking water.

MATERIALS AND METHODS

Water samples were collected on an annual regular basis, before and after agricultural pesticide application, and levels of selected water contaminating pesticides were detected in the samples using instrumental (gas chromatography – mass spectrometry, GC-MS) and immunoanalytical (enzyme-linked immunosorbent assay, ELISA) methods. Prior to analysis, water samples were subjected to solid phase extraction (SPE) (Majzik-Solymos, 2001), and were detected by an ion trap GC-MS. Quantification of the samples was carried out by peak area using the external standard calibration. A calibration curve was obtained with pesticides standards in the range of 0,001–10 µg/l that extracted at the same conditions as the test samples. Immunoanalytical methods were used, in parallel, for the detection of acetochlor, fenoxycarb and trifluralin. These ELISA methods were previously developed in-house immunoassays allowing quantitative detection of these three active ingredients at 0.2, 0.11 and 0.25 µg/l, respectively (Hegedüs *et al.*, 2002; Le *et al.*, 2003; Székács *et al.*, 2003 and Hegedüs *et al.*, 2000).

RESULTS

Target pesticides were selected on the basis of their physico-chemical features, analytical detectability, and on the basis of the results of preceding surveys (Kárpáti *et al.*, 1998). Thus, the active ingredients including acetochlor, atrazine, carbofuran, fenoxycarb, diazinon, metribuzin, phorate, prometryn, terbutryn and trifluralin, were selected as target analytes for the present study.

Table 1 contains a summary of the occurrence and detection limits of these pesticides examined in samples collected during the three years study on Hungarian surface waters. Survey results indicated that detectable analyte levels were observed in approximately 60% of the collected water samples. Distribution frequency for these ingredients was as follows: acetochlor, 25%, atrazine, 17%, prometryn, 7%, diazinon, 6%, metribuzin, 6%, terbutryn, 2%, trifluralin, 1% while carbofuran, phorate and fenoxycarb were not detected in any sample. As seen from this distribution patterns, the two most abundant pesticide contaminants from the list of pesticides monitored are acetochlor and atrazine. Detected pollution in some cases did not correlate well with actual pesticide application (diazinon). Contaminations by acetochlor reached the alarming 2-3 µg/l level, and atrazine contaminations of agricultural origin also did not lag behind. At two locations, levels of both acetochlor and atrazine were far exceeding that attributable to agricultural origin: the sporadically detected 16-47 µg/l pesticide level in surface waters raise serious concerns in environmental and human toxicology.

Pesticide Active Ingredient	Surface Water Body (River/Lake) Sampled*	Number of Samples Collected	Detection Limit (DL) [ug/l]	Number of Positive Samples
Acetochlor	Duna	141	0,1	40
	Tisza	123		32
	Balaton	75		15
	Velencei	25		0
Atrazine	Duna	141	0,1	39
	Tisza	123		4
	Balaton	75		20
	Velencei	25		0
Carbofuran	Duna	141	0,5	0
	Tisza	123		0
	Balaton	75		0
	Velencei	25		0
Diazinon	Duna	141	0,05	6
	Tisza	123		11
	Balaton	75		5
	Velencei	25		0
Fenoxycarb	Duna	141	0,5	0
	Tisza	123		0
	Balaton	75		0
	Velencei	25		0
Metribuzin	Duna	141	0,1	6
	Tisza	123		14
	Balaton	75		1
	Velencei	25		0
Phorate	Duna	141	0,01	0
	Tisza	123		0
	Balaton	75		0
	Velencei	25		0
Prometryn	Duna	141	0,1	8
	Tisza	123		11
	Balaton	75		5
	Velencei	25		0
Terbutryn	Duna	141	0,1	3
	Tisza	123		0
	Balaton	75		1
	Velencei	25		0
Trifluralin	Duna	141	0,001	1
	Tisza	123		2
	Balaton	75		0
	Velencei	25		0

*Surface water bodies sampled included the rivers Duna (Danube) and Tisza, and lakes Balaton and Velencei-tó (Lake Velencei).

Table 1: Pesticides Residues in Hungarian Surface Waters during 2000 – 2002

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HCH POLLUTED SITES MANAGEMENT IN ALSACE (FRANCE): A CASE STUDY

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ABSTRACT

In 1966, 700 tons of HCH residue were dumped by a company producing lindane on a site in the Alsace region, France. In 1985, confinement works were implemented on the site. In spite of these efforts, groundwater pollution has been observed. Since January 2000, this site has been managed by the French Agency for Environment and Energy Management (ADEME). A study implemented in June 2002 enabled us to evaluate the extent of the pollution, to characterise the hydrogeological conditions of the site and the deposit, to study natural attenuation phenomena and to look at the different rehabilitation scenarios of the site.

KEYWORDS

Groundwater, HCH, management, pesticides, pollution, rehabilitation, sites, soils.

INTRODUCTION

The Alsace region is highly industrialised. During the 60ies and 70ies, some production plants of lindane (gamma-hexachlorocyclohexane isomer) were based in this region. Important quantities of lindane production wastes (alpha, beta, delta-hexachlorocyclohexane isomers) have been released in tanks or bulk in former gravel pits. The sites housing these wastes reach the number of ten. Among them, three have been considered as "sites with defaulting responsibility" since the 90ies. That is the reason all operations carried out on these sites (studies and rehabilitation works) are managed by ADEME with the agreement of the French Ministry of the Environment. These three sites present different characteristics at several levels: the amount of wastes, the former management of the storage (confined or not), the geographical situation (urban or industrial zone).

This article presents the actions led on an HCH storage site, covered by a compacted clay layer and situated close to an urban area of 67,000 inhabitants.

HYDROGEOLOGICAL CONTEXT

The Alsace region has a groundwater potential of 50 billions m³ over a 2,800 km² surface area. The water table is

shallow, located from a few centimetres to a few meters from the ground level according to the local topography and the aquifer recharge. The groundwater average velocity is about 1 to 8 meters per day. The Alsatian groundwater is both consistent and fragile. This water resource is very important for the region and highly abstracted (about 0,5 billions m³ per year).

SITE GEOLOGICAL CONDITIONS

This site is situated in an alluvial zone. These alluvions consist of sand, gravel, pebble and blocs surrounded by clay. The whole is stepped by a more or less sandy clayey layer. These more or less coarse deposits are also covered by leossic silt reaching an average thickness of 1 meter. The alluvial deposit on the whole reaches a thickness of 50 to 60 meters and lies on an impervious substratum. Below the site, the groundwater flows from west to east with an inflexion to northeast during periods of low water and to southeast during periods of high water. The groundwater table is locally situated at a depth of 13±2 m and the hydraulic gradient is around 1%.

HISTORY OF THE SITE

In 1966, about 700 tons of HCH powder residue were dumped on this site. Soon after this unloading, resident protests were registered and the sale of agricultural produce (milk, potatoes, etc) was prohibited because of the pollution of the surrounding soils by HCH powder that had flown off. Consecutively, the site has been used to dump various backfills. In 1974, the authorities decided that the site should no longer be designated for habitation. Between 1982 and 1984, the company liable for the pollution was bound by the authorities to carry out a study concerning the impact on the site and to make works destined to "definitively neutralise the deposit".

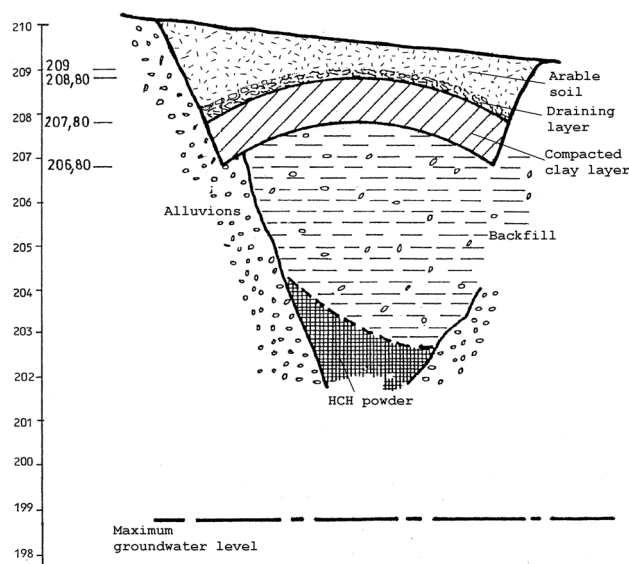


Figure 1: Clayey cover schema

The site was confined by the BRGM (French Institute of Geologic Research) in 1985. It consisted in the imple-

mentation of an impermeable cover made of compacted clay. The cover (Figure 1) consists of a dome of clay (about 5,100 tons) with an average thickness of 1 meter over a surface of 2,500 m². The compacted clay permeability reaches 5.10⁻⁹ m.s⁻¹. It is covered by a draining layer and arable soil. At the same time, restrictions concerning the use of the site were taken not to damage the impermeable layer: planting, irrigation and construction were forbidden.

GROUNDWATER QUALITY CONTROL

The first groundwater quality controls were implemented in 1972. They consisted of piezometric measures at the border of the site. The following controls were done in April 1986 (5 months after the implementation of the impermeable cover) and in May 1989. In spite of the dubiousness linked to the various analytical methods, the fact remains that the works implemented have had an influence on the amount of HCH contained in the groundwater. The report elaborated by the BRGM at the end of the works emphasises the fact that “the impregnation of HCH in the underground is so high that several years would be needed to regain a normal situation”. The water quality controls have been pursued more or less steadily since 1989 and carried out half-yearly between 1994 and 1998. But, contrary to the advice of the BRGM, the maintain of the site was not fulfilled during that period and shrubs, whose roots could damage the cover, had grown up. The authorities gave the company liable for the deposit formal notice to maintain the site and to carry out complete and steady groundwater quality controls. In January 2000, noticing the inaction of the company and its official receiver, they decided to entrust the implementation of operations to ADEME, at the cost of the liable company. Since then, the cleaning of the site has been done half-yearly and a net of piezometers has been set up, using either early wells or new drillings. Figure 2 shows the points of control, their implementation date and the average concentration since

their implementation. The results of the study conducted by ADEME show high concentrations of HCH in the groundwater situated right downstream the site, which led us to the conclusion that the cover implemented in 1985 may not be efficient.

Between November 2001 and January 2002, a survey implemented by the BRGM at ADEME's request enabled us to number the potential groundwater users situated downstream the site in 2001. 30 drillings have been listed near or downstream the site. In the sector of that study, only one drilling presents a hazard, since it is used for filling up a public swimming pool. This drilling (n° 94, Figure 2) is not exactly situated downstream the deposit, but HCH traces have still been found there several times. Complete and steady controls of the content of HCH in water sampled from this drilling are recommended in the report conclusions.

According to the HCH concentrations measured in the different piezometers, it was decided in May 2003 to set other piezometers over a zone situated between 1 and 2 km downstream the site (see Figure 2) for the evaluation of the pollution plume extent in the groundwater to be more reliable.

STUDY IMPLEMENTED IN JUNE 2002

In June 2002, the ADEME entrusted a study to the research consultancy HYDRO INVEST. This study aimed at several goals: Characterisation of the site; Characterisation of the hydrogeological conditions below the site; Characterisation of the pollution transfer mechanisms in the unsaturated zone as well as in the saturated zone; Characterization of the extent of the HCH pollution plume in the groundwater; Inventory of the different techniques that could be used to carry out the rehabilitation of the site and to make up for its impacts on the groundwater.

BORINGS AND DRILLINGS IN THE STORAGE ZONE

The aim of these borings was to characterise the extent of the HCH deposit and the state of the clayey cover. The boring techniques have been chosen in order not to damage the clayey cover and not to cause any prejudice neither to the residents (flying of HCH powder) nor to the groundwater. It led to the use of a mechanical auger, which did not need any drilling fluid but did not enable us to drill through when bumping into pebbles or big blocs. The drillings were systematically stopped when bumping into pure HCH powder. The position of the borings has been chosen according to the previous studies implemented in April 1974, October 1983 and June 1984. After their implementation, every drilling has been filled in again by spoil and a 2-meter-depth swelling clay. The main conclusions of HYDRO INVEST intermediate report after the operations are as follows:

- Some borings implemented on the borders and exterior to the cover present a distinct HCH smell, which means that the deposit is not completely covered by the clayey cover implemented in 1984.

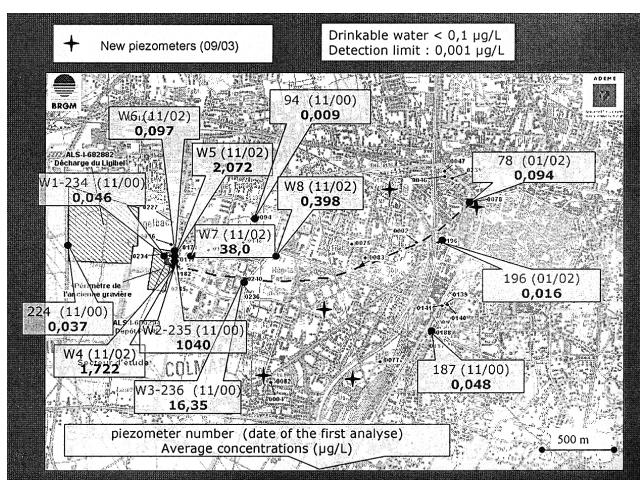


Figure 2: Piezometers situation map

- The clayey cover has been bumped into for several borings. It is very compact, dry or slightly wet. In the central zone, the cover crops out and its maximum thickness is between 1.4 and 1.6 m. On the borders its thickness is very unsteady, between 0.3 and 1.1 m. It seems to be gutter-til-shaped. According to its compactness, it seems very unlikely to be fissured or damaged by roots.

- The level of the soil covered by the clayey layer is lower than the surrounding lots, so rainwater can infiltrate into the soils surrounding this sinking area. Moisture has been noticed in the deposit as well as in the layers located at several meters in depth.

- Other borings have been implemented but provided very few information concerning the real depth of the deposit. During the drilling of piezometers W4 and W6b, the depth of the backfills did not seem to exceed 7 to 8 m (+ 201 to 202 m NGF). But, on the other hand, during the drilling of piezometer W1-234 (see Figure 2), backfills have been found down to 12 m, i.e. below groundwater level.

The groundwater circulating under the deposit is also highly polluted by a household waste landfill located 250 meters above the HCH deposit. An important mineralisation of the groundwater has been noticed ($> 2\text{g.L}^{-1}$).

MEASURES OF PERMEABILITY

The site permeability was measured using pumping tests in unsteady state. These tests were carried out on boreholes W5, W6, W7 and W8. The tests data were interpreted using the Jacob semi-logarithmic method. This method is based on Jacob's semi-logarithmic solution:

$$s = 0.183 \frac{Q}{T} \log\left(\frac{2.25Tt}{r^2 S}\right)$$

where s is the observed drawdown (m); Q is the pumping rate (m^3/s); T is the aquifer transmissivity (m^2/s); S is the storage coefficient (no dimension), R : observation distance (m).

As the pumping rates were variable, interpretation was made according to the specific drawdown s/Q :

$$\frac{s}{Q} = \frac{0.183}{T} \log\left(\frac{2.25Tt}{r^2 S}\right)$$

The transmissivities deduced from these tests range between $3.10^{-4} \text{ m}^2/\text{s}$ to $3.10^{-3} \text{ m}^2/\text{s}$. The site permeability (K) was deduced from transmissivity (T) using the expression $K = T/e$, where e is the aquifer saturated thickness ($e=50\text{m}$ at the site).

Estimated permeability values are included between: $10^{-4} \text{ m/s} < K < 10^{-5} \text{ m/s}$. The permeability of the site is rather low and can be explained by the importance of the clayey fraction within the alluvial formations.

ANALYSIS ON SOLIDS

Three samples have been analysed:

White HCH powder: This powder is not pure, but is mixed with minerals. It contains only 24.6 g.kg^{-1} and 1% of metabolites (mainly tri and tetrachlorobenzene). It presents a very strong smell. Its HCH composition is distributed as following: 27.5 % of alpha-HCH, 31.9 % of beta-HCH, 15.4 % of delta-HCH, 25.2 % of gamma-HCH.

Grey clay: The HCH powder is not visible, only its smell shows its presence. The global HCH concentration is 5.6 g.kg^{-1} and the amount of metabolites is 6 %. The distribution between the various isomers is different from that of the powder: 46.5 % of alpha-HCH, 1.2 % of beta-HCH, 32.8 % of delta-HCH, 19.4 % of gamma-HCH.

Clayey soil: The HCH powder is not visible, only its smell shows its presence. The global HCH concentration is 1.15 g.kg^{-1} and the metabolites are almost non-existent (0.1 %). The distribution between the various isomers is still very different: 95.1 % of alpha-HCH, 2.1 % of beta-HCH, 1.4 % of delta-HCH, 1.4 % of gamma-HCH.

EXPERIMENTAL PROTOCOL TO EVALUATE NATURAL ATTENUATION PROCESSES

Laboratory scale experiments are being processed in order to determine the HCH retention capacity of the soil and its capacity to be the location of their biodegradation.

For this, "clean" soil has been taken on the site and got in touch with highly contaminated groundwater from the piezometer W2-235. Six identical samples have been prepared and placed in a 12°C room (temperature of the groundwater).

After each of the six incubation periods (1, 4, 15, 30, 45 and 60 days), the four HCH isomers, chlorobenzene isomers, phenols, chlorophenols, mineral components as well as fatty acids will be analysed for solid materials and water. pH, redox, conductivity and the solute oxygen level will also be measured in the water. The results of these experiments will be available in September 2003.

NUMERICAL MODELLING

Tracing test and transport parameters determination

A tracing test with fluorescein was carried out in February 2003 in order to determine dispersivity and effective porosity of the aquifer. Fluorescein was used as this is a conservative tracer. It took place in two boreholes (W6 and W6bis), 30 m distance from each other. A pumping was done on W6bis till it reached a steady state. Afterwards, 1 kg of dissolved fluorescein was injected in borehole W6. The test lasted over 254 hours, divided into three parts: i) pumping during 41 hours with a discharge of $8 \text{ m}^3/\text{s}$, ii) 50 hours stop due to a pump breakdown, iii) pumping during 163 hours with a discharge of $13 \text{ m}^3/\text{s}$.

This tracer test was interpreted using numerical modelling. Analytical solutions are indeed valid only if the test is done in steady state. The digital model is represented in Figure 4. Cells having 1 meter dimension and 20 cm around

the boreholes W6 and W6b should be sufficiently precise and close to field reality. North and south borders are no-flow boundaries, east and west borders are constant head boundaries. Interpretation was made using the PMWin® platform. This platform comprises in particular MODFLOW and MT3DMS software, which numerically solve the flow and transport equations. The flow equation is the following:

$$\frac{\partial}{\partial x} \left[K_x \frac{\partial H}{\partial x} \right] + \frac{\partial}{\partial y} \left[K_y \frac{\partial H}{\partial y} \right] + \frac{\partial}{\partial z} \left[K_z \frac{\partial H}{\partial z} \right] - Q = S_s \frac{\partial H}{\partial t}$$

where K_x , K_y , K_z are components of the saturated hydraulic conductivity [L.T-1]; H is the hydraulic head [L]; Q is flow per unit volume and time (sink/source term [T-1]; S_s is the specific storage coefficient [L-1].

The transport equation writes:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial C}{\partial x_j} \right) + \frac{\partial}{\partial x_i} (u_i C) + \frac{q_s}{\omega} C_s - \frac{\rho b}{\omega} \frac{\partial \bar{C}}{\partial t} \frac{\partial C}{\partial t} - \lambda \left(C + \frac{\rho b}{\omega} \bar{C} \right)$$

where C : contaminant concentration [M.L-3]; C_s : sink/source concentration [M.L-3], concentration of pollutants adsorbed on the porous material [M.L-3]; x_i : distance according to the X axis [L]; D_{ij} : hydrodynamic dispersion coefficient [L.T-1]; u_i : pore velocity according to axis i [L.T-1]; q_s : sink/source term (per unit volume) [T-1]; ω : kinematics porosity [-]; ρb : density [M.L-3]; λ : kinetic constant of first order reaction [T-1].

The simulated breakthrough curve is shown on Figure 3 (concentration is in kg.m-3, time in hours). The deduced transport parameters are: effective porosity = 20 %, longitudinal dispersivity $L_L = 10$ m. transverse dispersivity L_T is generally taken equal to one tenth of L_L . These parameters will then be introduced into the final model.

Hydrodynamic digital model of the site

The first step of model definition is to determine the boundary conditions. The extension of the site was selected relatively vast in order to avoid any side effect and any interference near the pollution site (see Figure 7). The boundaries are the following: the upstream limit corresponds to the head $H = 205$ m of the reference water table, the downstream limit corresponds to river downstream the city, the southern limit and partly the northern limit are no-flow boundaries deduced from the reference water table, the linear limit to the northeast was located in order to extend to the maximum of the modelled field. This field was shared in square cells of 50 m by 50 m, in order to be able to account for heterogeneities of the alluvial aquifer.

Simulation was done with MODFLOW. The simulated water table is shown in Figure 4. The validity of the model calibration is checked by comparing observed heads on

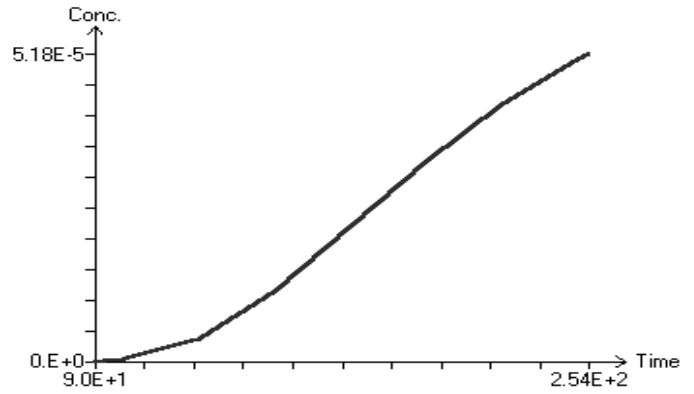


Figure 3: Simulated breakthrough curve using the model

available boreholes and simulated heads at these same points (see Figure 5). This figure clearly shows that the model is well calibrated in steady state. Simulated heads are very close to observed heads (coefficient of determination R^2 very close to 1).

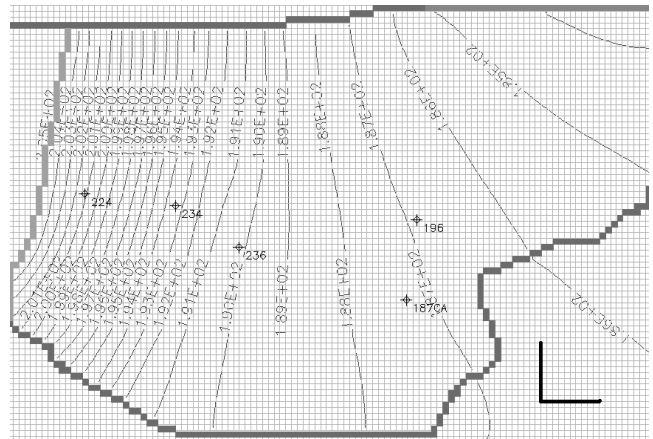


Figure 4: Numerical model of the site and simulated water table

The works in progress are related to the development of the unsteady model over the whole period during which the aquifer contamination took place, i.e. since 1966. However we are faced with a problem of lack of data. Meteorological data (rain, ETP) are available since this date. The water table fluctuations are only known on very few points during much shorter periods (two to 15 years). The work in progress tries to establish relations (statistical and/or empirical) to reconstitute reliable water table series over the whole period (i.e. 1966 to 2002). Following this work, the unsteady model will be developed in the most realistically possible way, in particular by introducing variable boundary conditions.

The aquifer contamination by the lindane deposit could then be simulated. Some batch tests are in hand to appreciate the natural attenuation of this product. These test results will be used to enhance the numerical pollution model of the site.

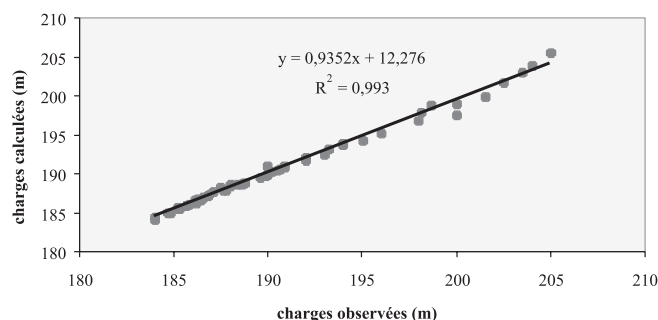


Figure 5: Steady state calibration of the numerical model: calculated versus observed heads

DIFFERENT POSSIBLE SCENARIOS

At the end of the present study of the site, several rehabilitation scenarios will be examined and interpreted: the removal of HCH residues, the implementation of a second larger clayey cover and the implementation of a hydraulic barrier. However, any of these solutions will be technically difficult to implement anyway and strong security meas-

ures will definitely be needed regarding to the proximity of the habitations by the site.

CONCLUSIONS

Many questions concerning the HCH behaviour in the saturated and unsaturated zones of the soil remain today.

How can we explain the different HCH isomers distribution in soil and groundwater? Why the cover does not completely fulfil its function? Do HCH residues buried in the deepest zone soak in the groundwater? What influence has rainwater? Are there any lateral or vertical water infiltrations in the HCH residue deposit zone? What is the amount of HCH participating to the groundwater pollution? What is the influence of the natural attenuation with the HCH concentrations measured in groundwater? Will the different rehabilitation solutions be efficient at long, middle or short-term concerning the quality of the groundwater? Are the soil and the polluted water secondary sources of pollution?

All these questions remain unsolved today but must be answered during the last months of the study implemented by HYDRO INVEST.

PESTICIDE'S ENVIRONMENTAL IMPACT ASSESMENT BASED ON ACCEPTABLE DAILY INTAKE (ADI)

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Problems of pesticide safety draw the attention of numerous scientists due to their high biological activity, progressive expansion of application in many countries, distribution over vast areas, persistence in the environment, ability to be accumulated in biological and water-food chains, and ability to penetrate into a human organism via food chains of plants, animals as well as via water, and air.

Scientific researches conducted focused currently on studying the following pesticide problems:

- Sources of pesticide's release into environment
- Chains in the environmental and transformation
- Methods for reduction and/or elimination
- Impact on human health and the environment

Due to their high toxicity, ability of lagging effects and high stability in the environment, some pesticides are in particular dangerous to the human health. Such substances

belong to so-called "Persistent Organic Pollutants" (POPs). The high risk of POPs has caused broad awareness in many countries across the world and has resulted in planning and acceptance of special measures at the national, regional and international levels focused on protection the health of population and the environment.

According to the UNEP decision an estimation of risk for the twelve most dangerous chemical compounds have been conducted. Those compounds include nine pesticides (DDT, Aldrin, Dieldrin, Endrin, Chlordane, Heptachlor, Hexachlorbenzene, Mirex, and Toxaphene) which are forbidden to use in Ukraine. Expert group formulated by UNEP developed scientifically based criteria and procedures for detecting POPs. At the session held in Stockholm on May, 22-23, 2001 the Convention on Persistent Organic Pollutants was accepted. Formulated criteria for POPs revealing and their environmental impact management are presented as follows:

Persistence is evidence that half-life of chemical substance is longer than two months in water, or is longer than six months in soil, or is longer than six months in sediment.

Bio-accumulation is evidence that bio-concentration factor or bio-accumulation factor in aquatic species is bigger than 5000 for the chemical substance or that Log K_{ow} is bigger than 5

Potential for long-range environmental transport is measured by level of chemical substance in selected location that has a potential concern from sources of release

Adverse effects - evidence that adverse effects for human health or for the environment; toxicity or ecotoxicity data that indicates the potential risk for human health or for the environment.

According to the generally accepted approach, the most important integral toxicological criterion is the acceptable daily intake (ADI), which is calculated based on the lowest no effect level of the limited criteria. The ADI is the maximum dose of a pesticide, estimated as a daily intake that could not cause any illnesses, or health deviations, or have effects on future generations during the lifetime.

It is obvious, that different pollutants have a different impact for same region and can have different effects in each particular case. This is the reason to use the hygienic criteria in the hazard evaluation of pesticides. (Figure 3)

The aforementioned criterion reflects a potential hazard. It is necessary to calculate the actual dose of pesticides organism receives from water, air and food for the evaluation of their real hazard.

We consider the possibility to attain ADI as a basic criterion of real hazard of each pesticide.

The general formula to estimate the actual pesticide dose (D_a) is:

$$D_a = \frac{D_1 + D_2 + D_3}{I} \quad (1)$$

Where:

D_1 = daily pesticide dose, received through food, mg;

D_2 = daily pesticide dose, received through drinking water, mg;

D_3 = daily pesticide dose, received through ambient air, mg;

I = average human weight (in the selected group of people), kg.

The common pesticide dose, received through food (D_1), is calculated by summarizing the amount has been found in separated products which are reflected an average consumption diet for the selected group of people:

$$D_1 = \sum N \cdot Q_i \cdot (1 - q_i) \quad (2)$$

Where:

N_i = pesticide concentration in product, mg/kg;

Q_i = amount of product in average consumption diet for one day, kg;

q_i = factor of pesticide destruction during the product cooking process depending on the available information; if information is not available $q = 0$.

The intake of pesticide from drinking water (D_2) can be described as following:

$$D_2 = N_w \cdot R \quad (3)$$

Where:

N_w = pesticide concentration in drinking water, mg/L;

R = daily intake of drinking water, L

For defining the pesticide dose receiving by the human organism through ambient air (D_3), the following formula is used

$$D_3 = T_o \cdot N_v \cdot V \cdot b_v \quad (4)$$

Where:

T_o = oral/inhalation factor for pesticide;

N_v = pesticide concentration in ambient air, mg/m³;

V = daily human respiration value, m³;

b_v = factor of pesticide absorption in a respiratory tract.

Analysis of data obtained in different agricultural regions shows, that D_1 forms 70-90 % of D_a , D_2 some 10-30 % and D_3 forms 3 - 10%.

The possibility of pesticides to attain the AEI (actual exposure index) is estimated in such way:

$$AEI = \frac{D_a}{ADI} \quad (5)$$

Where:

AEI = Actual exposure index.

The level of AEI may be observed as a basis for determination the pesticide pollution priority. To illustrate this fact we have researched three important pesticide pollutants in Ukraine are classified as POPs: 2,4-D (broadly used herbicide), DDT, and HCH. All examples were collected in the north part of Ukraine which is typical agricultural area and reliably reflect a real situation in the region. Two food products with most homogeneous levels of pollution which are milk and grain culture were chosen for calculation of ADI and AEI.

Received results are presented in Tables 1-3. For adult person daily consumption of water reach – 3 liter, volume of inhaled air – 20 m³, weight of consumed milk and dairy products – 1.225 kg, grain products – 0.38 kg.

Table 1 shows the total daily intake of pesticides residues from various sources (air, water, food) taking into account the contents of pesticide and daily intake may reach 0.0063 mg. The largest quantity of pesticides is taken into the person's body through the foodstuff and ambient air. Taking into account an average weight of an adult person some 60 kg the AEI factor is estimated at a level of ADI. It testifies the potential danger of these pesticides.

As it is evident from Table 2, the total daily intake of DDT residues from air, water, foodstuffs may reach 0.0671 mg. The largest quantity of pesticide is taken into the human body through the ambient air. Taking into account weight of body of adult person some 60 kg the AEI factor will be only a small part of ADI.

	Pesticide concentration	Daily consumption	Daily dose (mg/kg)
Water	0.0001 mg/ l	3 liter	0.0003
Air	0.0001 mg/m ³	20m ³	0.002
Milk and dairy products (in recalculation on milk)	0.0005 mg/kg	1.225 kg	0.000613
Grain products (in recalculation on flour)	0.009 mg/kg	0.38 kg	0.00342
Da	0.000106		
ADI	0.0001		
AEI	1.06		

Table 1. ADI and AEI calculation for 2,4-D

	Pesticide	Daily concentration	Daily dose (mg/kg)
Water	0.0001 mg/ l	3 liter	0.0003
Air	0.003 mg/m ³	20 m ³	0.06
Milk and dairy products (in recalculation on milk)	0.004 mg/kg	1.225 kg	0.0049
Grain products (in recalculation on flour)	0.005 mg/kg	0.38 kg	0.0019
Da	0.001118		
ADI	0.02		
AEI	0.06		

Table 2. AEI calculation for DDT

	Pesticide concentration	Daily consumption	Daily dose (mg/kg)
Water	0.0001 mg/ l	3 liter	0.0003
Air	0.004 mg/m ³	20 m ³	0.08
Milk and dairy products (in recalculation on milk)	0.002 mg/kg	1.225 kg	0.00245
Grain products (in recalculation on flour)	0.002 mg/kg	0.38 kg	0.00076
Da	0.001392		
ADI	0.001		
AEI	1.39		

Table 3. AEI calculation for HCH

Pesticide	AEI
2,4-D	1.06
DDT	0.06
HCH	1.39

Table 4. AEI overview

Case when AEI more or equal 1	hazardous pesticide
Case when AEI less that 1	low hazardous pesticide or pesticide when additional criteria for hazardous evaluation needs to be used

Table 5. Criteria for categorization

Table 3 shows that the total daily intake of residues of HCH from various sources (air, water, foodstuffs) may reach 0.0835 mg. The largest quantity of pesticide is taken into human body through the ambient air. Taking into account weight of body of adult person some 60 kg the AEI factor will be bigger than ADI. It testifies the potential danger of this pesticide.

The final results of AEIs are presented in Table 4

From data presented in Table 4 it can be concluded that possibility to attain ADI for DDT is negligible. At the same time, there is a real opportunity to attain ADI for HCH. The problem arising from environmental pollution from this compound is obvious. Such a situation can be explained by the wide application of HCH in former USSR. Application of HCH was banned in 1987 but in reality this pesticide was

used till middle 90-th. DDT has not been in use in Ukraine since 1969.

Finally, environmental pollution after 2,4-D seems also to be realistic. This fact is evident if the used quantity of this pesticide is taken into consideration. In 1999 this pesticide was used on 5530 thousand ha of land in Ukraine (total agricultural area is estimated in 28890 thousand ha) in number of some 7450 thousand tons.

The pesticide pollutants can be divided into two conditional categories based on AEI approach as it is indicated in Table 5.

It is obviously that urgent actions should be undertaken in order to reduce the potential impact of pesticides included into first category.

SUMMARY OF SESSION ON WASTE MANAGEMENT

Jesper Skårup and Kaare Helge Karstensen

Croplife International informed about ongoing empty container policy in four countries in an attempt to avoid further on-farm stockpiling of expired pesticides. Croplife had no immediate plans to expand its activities within empty container policy to the CEE region;

Mr. Ruban (environmental consultant) outlined specific experiences from an industrial remediation of HCH in Germany.

In Moldova the ongoing POP Enabling activity "Preparation of National Implementation Plans" are well under way and the estimated 6,000 tones of obsolete pesticides products are scheduled to be factored into the national solution following the outcome of the NIP process;

From Bulgaria, the Ministry of Environment and Water informed about ongoing long-term containment of obsolete pesticides through the national evened Balbok principle. Furthermore, the management of obsolete pesticides will become an integrated part of the scheduled 12-country pilot project operated by UNEP under the GEF POP Enabling Activity programme;

Tauw (Dutch consulting company) presented a recent developed WIM system (Waste Information Management) which based on FAO OPE developed templates for inventorying, enables national or regional authorities to keep and process key data on obsolete pesticides management;

The Norwegian Foundation for Scientific and Industrial Research (SINTEF) outlined major findings and lessons learned from developing a national plan for hazardous waste management in Vietnam also factoring in obsolete pesticides products.

THE AVOIDANCE OF ON-FARM STOCKS OF UNWANTED CROP PROTECTION PRODUCTS

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INTRODUCTION

The reasons for the accumulation of obsolete stocks of crop protection products have been well documented. In the two regions of the world where obsolete stocks are receiving most attention, in Africa and in Eastern Europe, the stockpiles have arisen from the poor management of stocks owned by governments or parastatal organisations compounded by an oversupply or an overproduction of crop protection products, in excess of farmers' needs or in excess of the capacity of the national infrastructure to deliver these products to farmers in a timely manner.

The transformation from central purchase to market economies has significantly reduced the potential for the accumulation of government-owned obsolete stocks in the countries of East and Central Europe, and also in Africa. All evidence confirms that a private market system effectively manages stocks in the distribution chain, because private enterprises thoroughly check the product needs of farmer customers, manage the level of stocks to an appropriate minimum and adjust supplies to meet seasonal demands. This view is substantiated by a recent ECPA survey in the EU accession countries, indicating no significant new amounts of obsolete stocks have occurred since those countries adopted market economies.

In recent years international meetings on this issue have focussed on the large quantity of state-owned obsolete stocks in countries in economic transition. At the same time, however, significant progress has been made in OECD countries in disposing of the much smaller quantity of obsolete or unwanted stocks held by farmers.

DISPOSAL OF ON FARM OBSOLETE STOCKS

Stocks of pesticides may accumulate on farms for a variety of reasons, for example non-appearance of expected pests, change in pest sensitivity to the active ingredient requiring a change in product, withdrawal of registration of the product or the introduction of use restrictions rendering the stock unusable for the purpose that it was originally purchased, damage due to freezing, changes in cropping patterns and others.

Some examples of schemes currently underway to collect and dispose of farmer owned obsolete crop protection products are as follows.

In Canada, the Obsolete Pesticide Collection Program "Operation Clean Farm" started in 1998 and is systematically covering all the agricultural regions. About 75% of the country has been covered and it is expected to complete the program in 2005.

To date, 508 tonnes of obsolete products have been collected and destroyed by high temperature incineration in Canadian incinerators.

The program was initiated and has been led by CropLife Canada, the national industry association, together with a series of multi-stakeholder committees, one in each province. Stakeholders include representatives from Provincial and Federal Departments of Agriculture and the Environment and Agricultural officials, retailers and grower groups as well as CropLife Canada.

A key element of the program is multi-media coverage to inform farmers of the opportunity for the surrender of obsolete product at no cost - apart the cost of transport to the collection site.

In Australia, "ChemCollect", a once-only scheme operated by the commonwealth and State governments, has collected approximately 2000 tonnes of obsolete products during the last two years, many of which have not been used since the 1970s. The scheme is free to farmers. ChemCollect is part of the Australian and New Zealand Environment and Conservation Council's *National Strategy for the Management of Scheduled Waste*.

To ensure that stocks do not build up again in Australia, the agriculture industry has agreed to institute ChemClear - an ongoing program for regular collections of registered farm chemicals which are otherwise non-returnable. ChemClear will begin early in 2004. ChemClear is a joint initiative involving Avcare (the National Association for Crop Protection and Animal Health) and a member of CropLife International, the Veterinary Manufacturers and Distributors Association (VMDA) and the National Farmers' Federation (NFF). The program is an example of industry's recognition of its 'cradle to grave' stewardship commitment for its products.

In France last year, industry, represented by the Unions des Industries de la Protection des Plantes (UIPP - a member of The European Crop Protection Association), working with a large multi-stakeholder group, have formed an operational structure 'ADIVALOR' to facilitate the disposal of obsolete stocks and used empty containers. 1000 tonnes of obsolete products have been collected to date.

In the UK, the Crop Protection Association, another EACA member association, and other stakeholders, have come together to implement the 'Voluntary Initiative', a package of measures that could be used to achieve the environmental benefits sought by Government as an alternative to a pesticide tax. Part of the proposals, now accepted by the UK government, includes a National Pesticide Retrieval Scheme for the disposal of unwanted and unapproved products. Many products will become illegal after 31st December 2003 and some products not used up this season will effectively become obsolete.

A PREDICTABLE LEGISLATIVE FRAMEWORK

A similar risk of obsolete stocks generation potentially exists for the accession countries joining the EU in 2004, at which time they will adopt the EU Directive 91/414/EEC regulating the registration and sale of crop protection products. This will inevitably lead to removal from the market of a considerable number of crop protection products that are currently authorised within the accession countries. Generation of new obsolete stocks could arise if the governments of these countries do not provide reasonable sell-out and use up periods for the products likely to be affected by the changes in legislation.

INCENTIVISING THE SURRENDER OF OBSOLETE STOCKS

Prior to the introduction of the collection schemes referred to above, farmers with obsolete stocks had some difficulty in finding a safe way of disposing of the materials. Obsolete pesticides are internationally classified as toxic waste normally requiring specialised disposal through high temperature incineration or other well regulated and monitored operations. The logistical difficulties of transporting to and receiving at such incineration facilities means that this is not a process suitable for small quantities of toxic waste. These schemes, and others in operation around the world, therefore provide farmers with a convenient and safe way of disposing of obsolete products. For the farmer, the 'at no cost' principal currently operating in most schemes provides the incentive to surrender product to the scheme rather than 'spraying off' the unwanted product onto suitable waste land, which is increasingly difficult to find or dumping the product at an inappropriate waste site.

However, obsolete stock collection and disposal is invariably expensive, so there is a clear incentive for both farmers and industry groups to avoid the accumulation of stocks both on farms and in the chain of distribution from factory to retailer. Stocks of unused products also represent an unnecessary drain on working capital. Minimising stocking levels therefore has clear financial advantages and has led, of course, to the 'just in time' principle of component supply in manufacturing. In developed private market economies, modern customer supply techniques now substantially reduce the necessity for farmers to carry on farm stocks of crop protection products.

GOOD PRACTICE

The principles of Good Agricultural Practise and Integrated Crop Management not only provide farmers with the techniques for the safe application of crop protection products, they also contribute to the avoidance of obsolete stock accumulation by, for example:

- Reducing difficulties with disposal by minimising waste production.
- Ordering enough product to do the job in hand and no more;
- Buying products in the largest practical container sizes;
- Storing products in good order;
- Choosing products which minimise or eliminate contaminated packaging waste;

- Keeping careful records of the movement of stock in and out of the agrochemical store; rotating stock on the "first-in, first-out" principle

- Never pouring pesticide in any form (including pack washings) into public sewers, drains, ditches or rivers etc.
- Adopting appropriate anti-resistance strategies and respecting label rates of use to ensure continued product effectiveness.

USED CONTAINER MANAGEMENT

Packaging and empty container waste is sometimes erroneously referred to as obsolete stock. The management of empty containers is a separate activity for farmers, with roles for local authorities and industry. The issues to be tackled in disposing of empty pesticide containers vary around the world. In many developing countries, small-holder farmers see the empty container not as waste, but as a useful item which they purchased with the product and they are reluctant to destroy it. Indeed the containers used by the majority of pesticide manufacturers are of high quality – robust, easy to pour from and leak-proof. Farmer training on the importance of triple rinsing of empty containers at the time of spraying, (with the rinsing water being added to the spray tank) and the avoidance of reuse of empty containers as water or food carriers is of great importance.

In countries where the waste disposal infrastructure - both in terms of expertise and facilities - does not exist, on farm disposal by burial or burning are the only practical options for safe disposal. In both cases triple rinsing and puncturing of the empty container is an essential requirement prerequisite. Designs and operating recommendations for efficient small-scale incinerators constructed from 200 litre drums are available from the British Crop Protection Association, from CropLife International and others.

In countries where the infrastructure exists for collection schemes to be a viable possibility, the possible final destination of the packaging material are:

- Landfill waste
- Recovery of steel from metal drums either for direct use or as scrap steel
- Energy extraction through combustion for burnable materials eg cement kiln fuel
- Recycling of plastic resins from high density plastic containers into appropriate products.

Recycling must be carried out using acceptable processes. In the United States, The Ag Container Recycling Council (ACRC), a non-profit organisation funded by about 30 member companies involved in the production, packaging, and distribution of crop protection products, accepts a number of uses for granulated plastic from clean pesticide containers, including:

- pallets
- construction site mats
- commercial truck/manure spreader decker boards
- field drain tiles/pipes
- speed bumps

- parking stops
- fence posts
- hazardous waste drums
- scaffold nailing strips
- commercial truck sub-floor support members
- sub-flooring/ supports for outdoor decking, steps, and walks
- marine pilings
- encapsulated wood substitute

In each case it has been established that the plastic resin will be used in such a way that any residues on or in it will have no real or perceived adverse effect on the environment or the user.

Collection schemes of this type normally accept only clean and drained containers. Eleven studies summarized in a US EPA Report to Congress, indicate that correct triple rinsing or pressure rinsing of empty containers, when carried out immediately the container is emptied, removes over 99.99% of the pesticide residues in the container.

Farmers in the United States use some 35 million plastic crop protection product containers a year. If laid end to end, these containers would line the route from Miami in the South

East United States to Seattle in the Northwest, across to Boston in the North East, and back again to Miami. In 2000, almost one third of these containers, more than 3000 tonnes of plastic, were collected in the U.S. to be recycled into a variety of useful products. In the same year Germany achieved a 45% recovery rate for used pesticide containers and Canada achieved a 67% recovery rate. In Australia, over 3 million containers have been collected in the agricultural industry drumMUSTER initiative since its commencement in 1999.

CONCLUSION

The above examples illustrate how the members of the CropLife International federation, through ECPA and other regional and national associations, are applying their expertise to the disposal and prevention of obsolete stocks and the reduction of chemical container waste. Many more initiatives than those discussed here are in operation and many others are being set up. All require a multi-stakeholder approach to be successful, but much progress in environmental protection can be achieved rapidly where the commitment of the stakeholders can be translated into practical solutions whilst maintaining high standards of safety.

MANAGEMENT OF INDUSTRIAL PRODUCTION SITES CONTAMINATED WITH HCH

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1.DANGER DUE TO HISTORICAL DEPOSITS

At one plant in Germany, Lindane was produced between 1954 and 1972.

Non-insecticide isomers were used – with approval of the authorities – to fill in ground affected by subsidence on the plant site. These filled sites are distributed over the entire plant.

2.OPTIMISATION OF MEASURES AS A RESULT OF DECADES OF EXPERIENCE

Even before production ceased, there were problems with drifting HCH onto adjacent agricultural land. Since then, all groundwork has been subject to restrictions imposed by the authorities. Thus, each year, millions have to be spent in certain cases in order to protect the residents around the plant.

More stringent environmental protection and occupational safety measures as well as the accompanying higher costs have brought about continuous optimisation of measures over the years.

The experience we have gathered over a long period of time has led to the procedures we use today.

All who have to cope with HCH problems can benefit from this success.

3.PERMANENT SAFETY MEASURES

Safety measures still have to be carried out even if there are no accidents; as this excludes any possibility of danger outside the plant.

3.1Securing hydraulic systems

As the ground water was contaminated by historical deposits, it was pumped out in such a way that the direction of flow was always towards the plant (Photo 1).

The historical deposit areas were sealed off from above in order to ensure that they were not transported to a deeper area by rainwater.

3.2 Biological purification of groundwater

Up to the mid-80s, HCH compounds were regarded as not being biologically degradable. However, by the end of the 80s, we succeeded in developing a practical process whereby larger quantities of contaminants could be reduced from ppm to ppt concentrations. As a result, the values lay under those of drinking water so that there was no problem in disposing of this in public water sources.

3.3 Washing facility

A washing facility was established for cleaning contaminated devices and vehicles. The water used is also treated biologically before being disposed of (Photo 2).

4.TYPICAL ACCIDENTS DUE TO HISTORICAL DEPOSITS

4.1 Rupture of supply lines

Major accidents occurred between the years 1995 and 2002. These were caused by the rupture of supply lines in

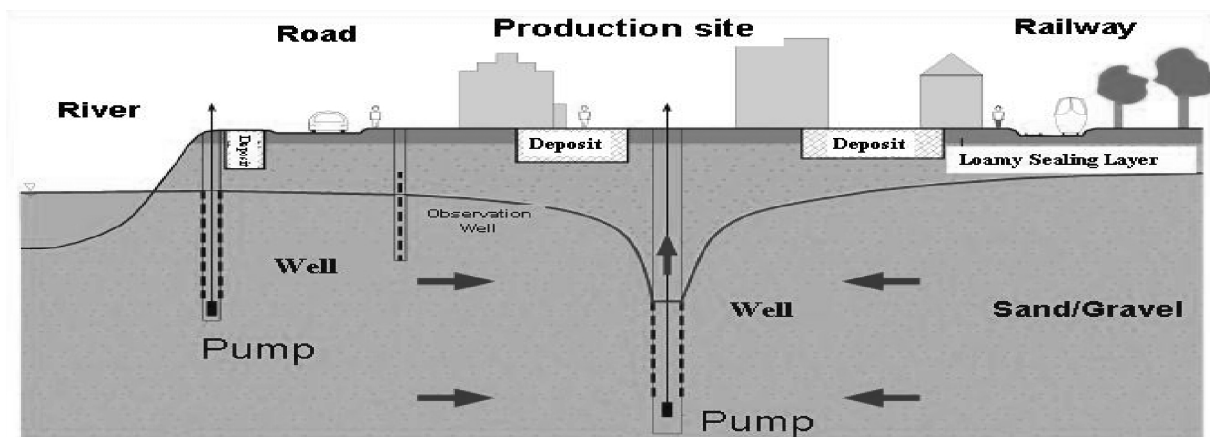


Photo 1

the area of historical deposits. The damage was mainly break-up of the road surface with leakage of pure HCH and contaminated water to the environment.

4.2 Construction work

In the course of carrying out road repairs, it frequently happened that non-charted HCH deposits were damaged

5. CONSEQUENCES OF ACCIDENTS

These accidents resulted in large quantities of contaminated water, soil and building materials (e.g. road surfaces, fundaments) being produced. Disposal of these cost several hundred thousands of Euros.

6. SAFETY AT WORK MEASURES

Contaminated areas are immediately sealed off so that no unauthorised persons may enter.

Protective walls are also erected in order to prevent drifting of contaminated material

The danger area may only be entered by authorised persons wearing full safety equipment (clothing and masks). There is a black-and-white area for such persons, reached only via a special lock.

The protective clothing is collected after each visit to the area and disposed of as special waste by incineration.

7. DEALING WITH CONTAMINATED WATER

There are two wastewater canal systems on the plant site. One leads directly to the wastewater treatment plant and the other directly to public waters. This second flow can be closed off at any time and redirected to the wastewater treatment plant.

The main problems concerned the fact that contamination could be carried over into the wastewater treatment plant and into the clarification sludge. On flushing out the piping system, excess levels of contamination were frequently observed over a period of weeks.

Today, the wastewater pipes are closed off at short notice by the fire brigade and directed into special reservoir basins. Activated charcoal is then used to decontaminate the water.

The water thus decontaminated and showing contamination levels below allowable values can then be fed into the



Photo 2

wastewater treatment plant, where activated charcoal is also used.

8. DISPOSAL OF CONTAMINATED WASTE

On-site fractionation of contaminated waste is particularly important; the higher the contamination the greater the cost potential for decontamination and disposal.

8.1 Washing waste material

Material that is only contaminated on the outside – building bricks, road construction materials etc. can be specially washed so that it can be disposed of as normal building material waste.

This external washing can be carried out on materials contaminated to the extent of 2%. This type of washing costs 100 EUR/t.

Material contaminated to a higher extent or contaminated with pure HCH can be incinerated externally. These costs are 150 -1.300 EUR/t.

9. LONG-TERM PERSPECTIVES

Longer term, it is planned to erect new buildings only on uncontaminated land. The land involved will be completely cleaned or replaced.

Thus, ultimately, although it may take some time, many areas will be designated as being clean.

Only such a step-by-step elimination of environmental contamination is ecologically meaningful and economically possible.

IMPACT OF PERSISTENT ORGANIC POLLUTANTS ON ENVIRONMENT AND HEALTH IN THE REPUBLIC OF MOLDOVA

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The assessment of pesticides inventories and impacts to date in Moldova is limited and would require detailed assessment. The following summarizes the current knowledge base on obsolete pesticides, including POPs, participation in the implementation of the Stockholm Convention, chemicals and waste management generally and the relevant existing regulatory framework.

Currently in Moldova approximately 6 000 tons of obsolete pesticides are stored in various former collective agricultural warehouses or disposed in controlled and uncontrolled dumps.

Most POPs pesticides, such as DDT, Aldrin, Toxaphene, and Chlordane are not produced, not used and prohibited since 1970-1972. At the same time that substances are not included in official register of permitted substances for use in agriculture, including and individual farms, forestry and household.

There are a number of specific activities and initiatives that have been undertaken at the national level to demonstrate country commitment to taking action on. These include:

- Elaboration and publication in 2000 of the National Programme on Production and Municipal Wastes

Management, which included some provisions to address obsolete pesticides, including POPs. This Programme was approved by the Government's Decision Nr. 606 from 28.06.2000;

- Elaboration and publication in 2001 of the Plan of measures on Centralizing Storage and Disposal of Obsolete Unused and Prohibited Pesticides. This Plan was approved 15 January 2001 (Government's Decision Nr. 30 from "On Measures for Centralizing Storage and Disposal of Obsolete Unused and Prohibited Pesticides");

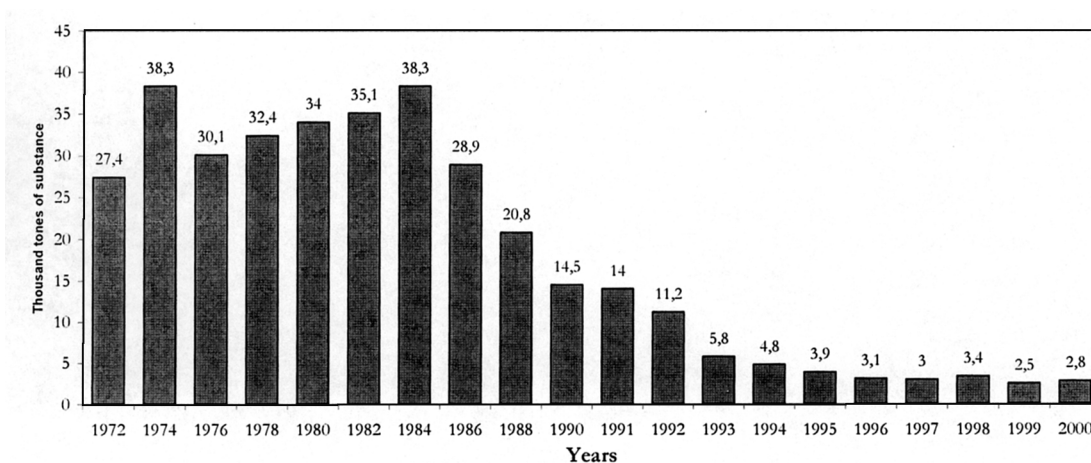
For the solving of the problem of obsolete pesticides and POPs in Moldova the Ministry of Ecology, Construction and Territorial Development applied for the support of the World Bank for the implementation of the Stockholm Convention. In April 2002 the project was approved and in July was signed the Grant for Preparation of Enabling Activities Related to the Implementation of the Stockholm Convention on the Persistent Organic Pollutants GEF-PPG with the total amount of 411,500 \$US for the duration of two years.

Impact of pesticides on environment:

- Information on the state, but not on consequences
- Information on quantities, but not on all types (up to 50% - unknown)
- Limited links between the impact on environmental components (soil, water, air) at the local, regional and trans-boundary context
- Lack of co-ordination between different monitoring and control institutions
- Average concentrations in soil and water last 5 years under the allowed limits.

Impact of pesticides on public health:

- According to the medical data, professional illnesses since the period of the former URSS
- Intoxication data from the agricultural sector mainly



Trend of use of pesticides in the Republic of Moldova

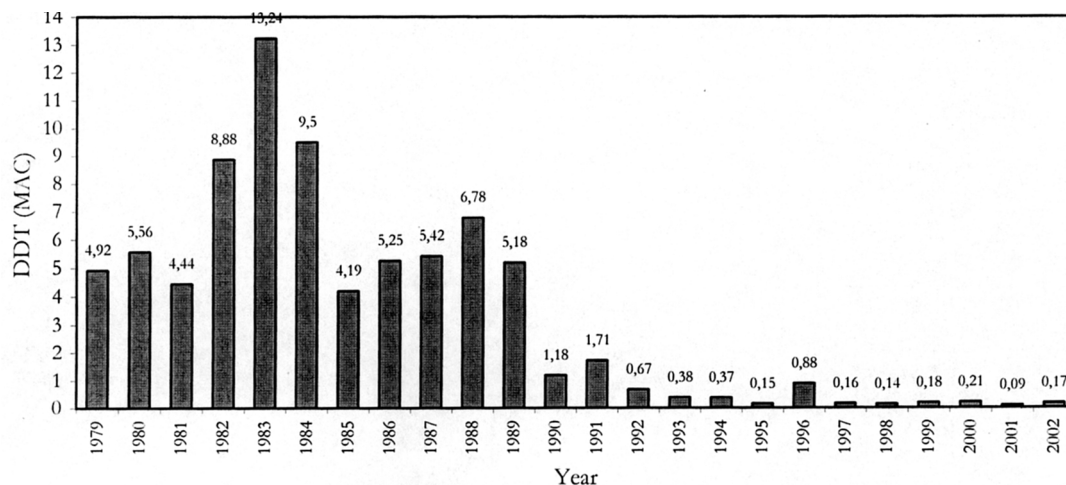
- Limited links between the impact on environment components (soil, water, air) and human health
- Indirect impact only on base of special studies
- Only exported products are tested on pesticides contamination, local consumption – without general control.

Expected Results of the WB project:

- Elaboration of National Implementation Plan

- A sustainable institutional framework governing the management of the POPs
- Enhanced capacity for implementation of related chemicals conventions in an integrated fashion with the Stockholm Convention
- Ratification of the Stockholm Convention by the Parliament of Moldova and the country being fully prepared for participation as a compliant party to the convention.

Annexes



Average level of DDT residues in soil



Photo nr. 1: Storage of the obsolete pesticides, Gratiesti, Chisinau County, Moldova

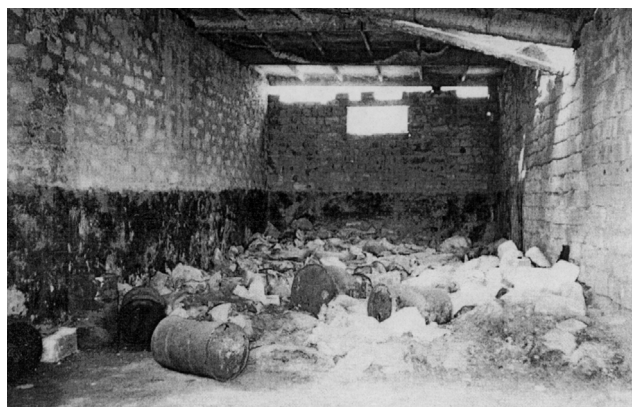


Photo nr. 2: General view of the warehouse of obsolete pesticides, Gratiesti



Photo nr. 3: Vulcanesti Pesticides dump, 4 000 tonnes of obsolete pesticides



RELIABILITY ASPECTS OF TREATMENT AND STORAGE OF OBSOLETE AND BANNED PESTICIDES – TECHNOLOGIES AND PRACTICES

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ABSTRACT

BalBok Engineering developed a universal technology for physicochemical treatment, safe long-term storage of obsolete and banned pesticides, and remediation of contaminated sites. This technology is based on proven results in the practice of radioactive waste management achievements. The licensed and standardised container B-B cube ensures safe long-term storage and disposal of the obsolete and banned pesticides®.

This technology has been implemented successfully in Bulgaria since 1998 and until now more than 5000 m3 obsolete and banned pesticides are treated according to it.

In development and implementation of this universal technology, the following principles were followed: ALARA, cost-effectiveness, investment rate, and public acceptance. Thus, a holistic approach is applied towards solving the problems caused by the widespread stockpiles with obsolete and banned pesticides.

INTRODUCTION

The 6-step technology /6ST/ presented in this paper is a result of seven years of scientific research, together with fieldwork, observations and analyses of the results. The technology is thoroughly based on the multi-barrier approach for environmental and human health protection from the adverse impacts of hazardous waste. The authors' more than 20 years of experience in research of highly toxic substances and radioactive waste management, provided the prerequisites for development of a new technology for obsolete and banned pesticides treatment and disposal. 6ST is result of an innovative, non-traditional understanding of the essence of the problems caused by the obsolete and banned pesticides and a new approach towards their treatment and disposal.

Obsolete pesticides – EHS (Environmental, Health & Safety) The obsolete pesticides appear in the form of either 1) powders, very often compacted to the extent that they are rock-like; 2) suspensions (water with solid pesticides or mixed solid (powders) and liquid pesticides); or 3) solutions (inorganic pesticides dissolved in rainwater).

The long-term bad housekeeping and storage of old pesticides created conditions for uncontrolled and unknown chemical reactions between their active ingredients. High summer temperatures and the water media catalyse these chemical reactions; at the same time the constant entering in the soil and water of the new substances prevents reaching equilibrium. As a result getting of the newly formed

chemical substances into the bio-cycle can have unpredictable sequels.

The accumulated in the past decades pesticides during their storage reached quantities and forms, which characterize them as widespread hazardous waste. The EHS problems coming from these stockpiles of unwanted obsolete and banned pesticides are:

- In most of the cases, the quantities in one store exceed hundreds of kilograms, what creates preconditions for emergencies.

- Unpredictable chemical composition due to retardation processes and chemical transformations that alter contaminants' type and concentration

- Toxicity
- Ignitability
- Corrosivity
- Reactivity
- Bio-accumulation



HAZARDOUS WASTE
CHARACTERISTICS

- Migration in soils - the old stores themselves very often present danger from collapsing and they do not protect the pesticides from rains and snowfalls thus creating conditions for contamination of soils and drinking water

- The safety issues arise from the fact that most of the old pesticides have the same or close chemical formula to chemical warfare agents. Thus, safety requirements should not be underestimated.

Undertaking steps for total inventory, which will provide data on the weight and volume of the stockpiles; type of the pesticides; their forms (solids, liquids, and suspensions); location; and type and scale of contamination of the adjacent to the stores territories, in most cases is impossible in short time and is economically unsound. Such an inventory requires both very well trained staff, equipment, new methods for quantitative and qualitative determinations of the products of the chemical reactions in the stockpiles, and to be reliable, it needs regular up-date.

Selection of a technology applicable to this widespread hazardous waste depends (besides economic issues and public perception) predominantly on its universalness and low dependence on the type of the treated pesticides.

OPTIONAL SCHEMES AND TECHNOLOGIES FOR OBSOLETE PESTICIDES MANAGEMENT

Until 1999 there were two main ways among all available [2] used to deal with old pesticides worldwide – thermal destruction of the active ingredients and disposal.

There are several thermal methods for waste treatment [5,7] – incineration, pyrolysis, gasification, and combination of gasification and pyrolysis are the most popular among them. Each of these processes has requirements about process conditions and generates different products.

Disposal is an operation that strongly depends on the characteristics of the site. There are examples proving that what had been initially considered as a barrier later on acts as media to spread the contamination into the environment. [6]

Figure 1 presents 3 possible ways for treatment and disposal of obsolete pesticides –thermal destruction, land disposal and 6ST.

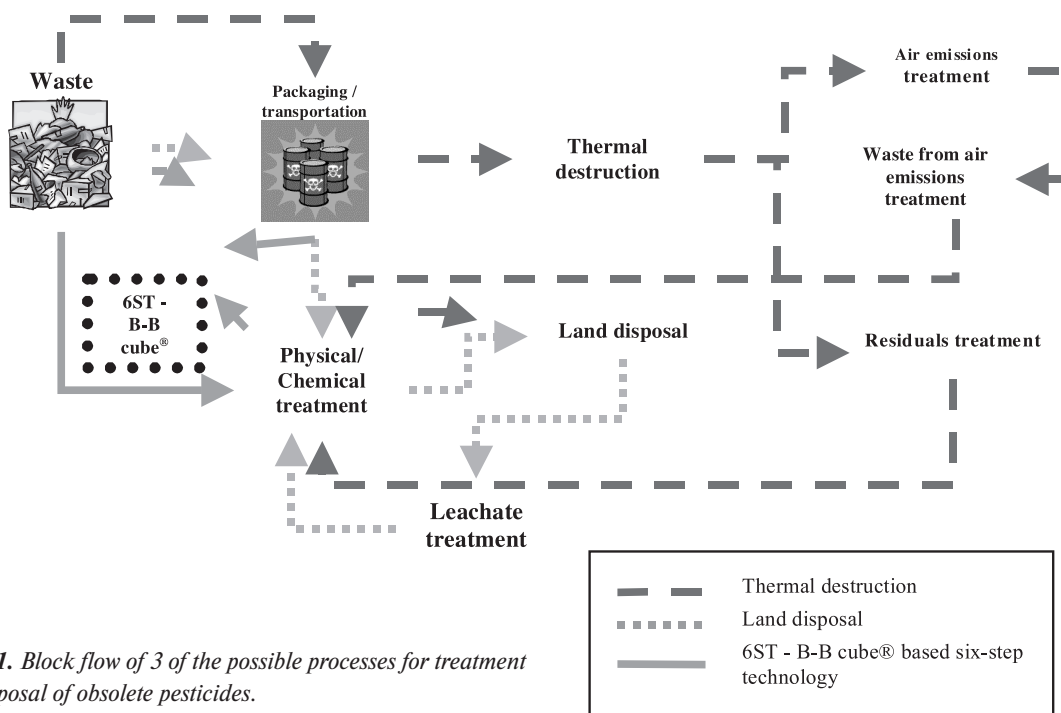


Figure 1. Block flow of 3 of the possible processes for treatment and disposal of obsolete pesticides.

The third option – 6ST – is to dispose of the obsolete pesticides after an adequate physical-chemical treatment in order to condition the waste before filling it in containers and placed on surface sites.

DESCRIPTION OF 6ST

6ST has been developed on the basis of the multi-barrier approach for protection of the environment and human health.[1]

It consists of the following 6 steps (which name is used):

Step 1

The first step includes:

- Estimation of the quantities of the waste at given location
- Preparation of the project's budget, together with logistics and risk assessment with an emergency plan

Step 2

Re-packaging of solid obsolete pesticides is the second step of the technology.

Step 3

The third step is in situ physicochemical treatment of obsolete pesticides, based on the universal solidification and stabilisation technology. The final product of this treatment is solid, with compressive strength of over 3.5 MPa and leachability under 1.10-2 g.cm/day.

The final product with its characteristics is the first barrier.

Step 4

This step consists of the following two operations:

- Filling B-B cube® containers with re-packaged and treated as described in Step 3 waste. The waste packages are placed in the container with sorbent.

- Sealing full containers and laying hydro isolation.

The capacity of the packaging complex is 5 m³ of waste. The overall weight is over 13 ton and it needs 4 m² for placement.

The requirements for the packaging complex are:

1. to provide opportunity for transportation and long-term storage (as a minimum of 100 years).
2. to be waterproof
3. to be resistant to temperature amplitudes from - 300 to +500C
4. to be bio-resistant (against fungi and bacteria)
5. to be seismo-resistant
6. to be fire-resistant
7. to allow maximum usage of the available space
8. to retain its integrity in emergency situations, such accidents during handling
9. to retain the content during the entire period of storage

Container B-B cube® is a specialised package for hazardous and radioactive waste, which meets all of the above requirements. Its technical and mechanical properties are proved by a series of tests before its standardisation and licensing. [4]

B-B cube® is the second barrier between the waste, the environment and people.

Step 5

The fifth step includes:

- Construction of a site (if needed) to place the filled containers (packaging complexes)

The site is designed for long-term surface storage of the packaging complexes. The legal requirements have to be followed during selection of the site location. In addition, it has to have a drainage system, and a monitoring every 6 months is necessary. The characteristics of the packaging

complex based on the universal technology for physico-chemical treatment and B-B cubes®, as package replaces the need to construct a special engineering facility.

- Placement of the packaging complexes on site.

Step 6

Removing and neutralising any harmful substances from the floor and walls of emptied stores and from polluted soil around the stores is very important for the technology. It includes:

- Cleaning and decontamination of the old store

It is done to prepare it for future usage or for demolition. Consecutive treatment with oxidising and reducing agents techniques are used. Thus, destruction of residues of any hazardous compound of all groups of pesticides is ensured. The reminders after treatment are collected and included in the 3rd step of the technology.

- The cleaned spaces and terrains around the stores are treated with catalysts, which accelerates destruction of the hazardous compounds by the UV rays.

- After the previous two procedures, the cleaned store can be demolished and send to a construction waste landfill or used for industrial purposes, e.g. to store new pesticides.

CONCLUSION

6ST is a technology implemented and proved in practice. The monitoring on more than 800 packaging complexes, which has contained more than 4000 m³ treated obsolete pesticides over the last four years, proved the reliability of this solution. Implementation of 6ST does not require electricity and water supply at the stores with stockpiled obsolete pesticides (which in most of the cases is not available in old stores, partially for safety reasons). On the other hand, the technology requires well-trained personnel. The packaging complexes are secure against unauthorised intervention. 6ST is well accepted by the public. It is an overall, complete solution of the problem related to the obsolete pesticides. Packaging complexes allow indirect utilisation. Based on their physical, mechanical and functional characteristics, the packaging complexes can be utilised as walls for landfills,

as well as landslides. In addition, unlike other technologies, 6ST can be applied solely or it can be incorporated in other technologies. Also, the containers B-B cube“ could be reused, where it is applicable. 6ST being very cost effective, very quick and at the same time reliable, fills a gap in the technological management of hazardous waste.

ACKNOWLEDGMENTS

The authors would like to express their gratitude to the Ministry of Environment and Water and Ministry of Agriculture and Forestry of Republic of Bulgaria. Due to the financial support provided by them since 1998, the problems related to stockpiled obsolete pesticides has until now been solved in more than 50 municipalities in Bulgaria, through the implementation of 6ST.

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INVENTORIES OF OBSOLETE STOCKS: THE INNOVATIVE INVENTORY PROGRAM WIM

Jan Betlem

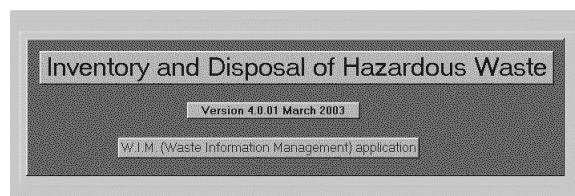
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WHAT IS WIM?

An inventory is the starting point and foundation of a workable clean-up plan. The scope of the problem has to be known before solutions can be developed (FAO Training Manual for Inventory taking of Obsolete Pesticides).

During the last decade, many countries have embarked on the detailed stocktaking of obsolete pesticides as a basis to formulate further actions. Although a standard FAO1 form is widely promoted, one of the problems was and still is in nearly all countries and organisations involved, that no computerised database is available in order to store the collected field data in a structural and retrievable way.

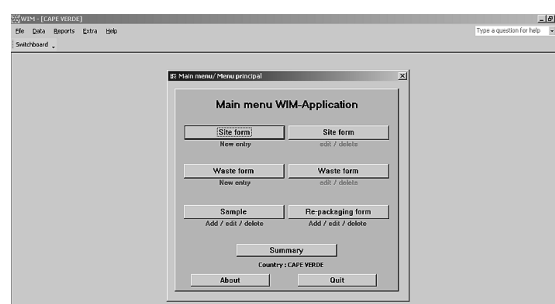
Developed in the field and tested already in various countries, Tauw has recently presented its **Waste Information Management (WIM)** database: A Microsoft Access database application based on the standard FAO forms.



WHAT CAN WIM DO FOR YOU?

Once you have collected the inventory data in the field and the standard FAO formats for each site and each identified waste per site have been filled in, the fieldwork can be considered completed. However, you still have no overview and analysis of the data, such as:

- What are the main wastes identified?;
- How much waste has been recorded? Liquid, solidified, solid, other?;
- What are the main manufacturers of the identified waste? (Important for potential co-funding);
- Do we have a few large sites or many small sites and where are the sites situated? (Important for logistics at a later stage in the project);



- Who are the legal owners of the observed wastes? (Important for legal ownership issues later in the project);
- What is the condition of the observed packaging materials? (Can the waste be transported? How should it be repackaged?);
- etc..

DATA INPUT

The program has several levels of data input according to the standard FAO inventory forms:

- Site information data (consisting of data about the respective site, such as environmental issues, ownership, condition of store, features of the store, etc.);
- Waste information (consisting of data about the identified and un-identified wastes within one particular site, such as trade name, name of active ingredient, quantity, package details, etc.);

Mfufu cturer	Active ingredient	Concentration	Site number			Form. Type	Toyal quantity	Trade name	P/V/I	Manufact.	Anival
not rele vant	not rele vant		19	D	1	Powder	1000 kg	contaminated dust from floor	P		
not rele vant	not rele vant		20	A	3		8 m³	empty packaging material	P		
Pechiney Procil	Parathion		18	B	3	Liquid	2000 litre	Parathion	P		
Pechiney Procil	Parathion		20	A	9	Liquid	510 litre	Ethyl pa pacathion	P		
Procida Groupe Roussel	BHC		19	A	6	Liquid	9000 litre	HCH	P		
Quino	Oxyquinoleine	140 gr/litre	21	A	15	Liquid	90 litre	Cryptonol	P		
Senchim	Dimethoate	400 gr/litre	21	A	8	Liquid	70 litre	Dimethoate	P	01-01-92	
Senchim	Endosulphan	350 gr/litre	21	A	9	Liquid	104 litre	Thiosulphan 25EC	P		
Shell Chemicals	Dieldrin		17	A	3	Solid	1250 kg	Dieldrin	P		
Shell Chemicals	Dieldrin		17	A	2	Liquid	1000 litre	Dieldrin	P		
Shell Chemicals	Dieldrin		17	A	1	Liquid	10000 litre	Dieldrin	P		
Shell Chemicals	Dieldrin		18	B	1	Liquid	9600 litre	Dieldrin	P		
Shell Chemicals	Dieldrin		19	A	1	Liquid	6600 litre	Dieldrin	P		01-01-65
Shell Chemicals	Dieldrin		19	A	2	Liquid	6000 litre	Dieldrin	P		
Shell Chemicals	Dieldrin		19	A	7	Powder	1000 kg	Dieldrin	P		

- Sample information (such as origin of the sample). The outcome of the laboratory analysis can later be imported in this form as well.

At a later stage in the cleaning-up project, data concerning re-packaging and transport to a central storage facility or even data related to the export to a final disposal facility can be included and re-called. This way, the Project Manager has a perfect overview of all involved sites and quantities of wastes including the movements of the wastes up to and including the final destination.

With WIM, manipulation of quantities and fraudulent reporting (for example by involved contractors and/or transporters) can easily be detected and thus avoided.

WIM can deal with data of several types of waste. The application can be used for data input and analysis of other chemical wastes (industrial wastes for example) as well as veterinary waste.

DATA MANIPULATION

Once data has been entered, it can be **edited or deleted**.

All three levels are interconnected with each other. For example it is possible to swop from a specific waste to the site information and vice versa.

The searchable database application can carry out all kinds of analyses and can present the outcome in tailor-made customer oriented tables. The outcome can be printed, or send in digital form by e-mail.

For users in need of producing an inventory output according to FAO format, WIM automatically prepares an Excel worksheet according to the generally used FAO format.

A search function is available to search for specific information. In order to obtain a quick overview, one option provides a summary of all data entered in the database. A GIS module has been attached to WIM in order to produce data in a GIS environment. Hereby, maps of the country or region involved - displaying the position of (selected) sites with custom-defined features and details - can be shown, printed, or pasted into reports.

Users have to log in with a username and password. Each user is a member of a user group with specific user rights for tables, queries, forms etc.

The required language should be selected during the log in. Currently, the main working screens (data input and data manipulation) of WIM are available in English, Spanish, French and Russian. More languages are expected to follow soon.

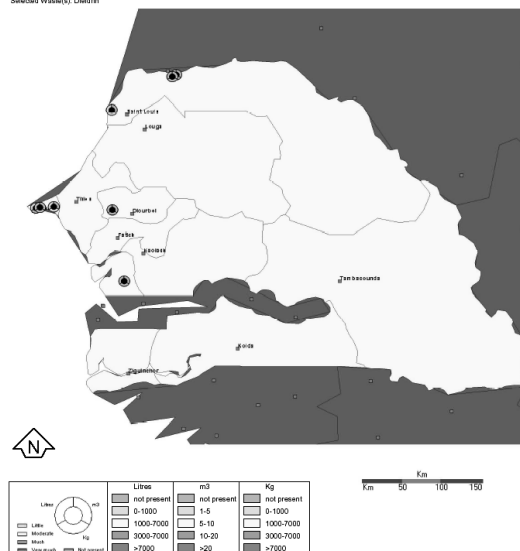
WIM IS EASY TO HANDLE

Experience has shown that WIM can be filled in during the fieldwork period. Immediately after fieldwork the data analysis can be made visible and printed out. WIM is not developed for scientific purposes: It is a practical tool to be used in the field and afterwards for the purpose of data analysis and the generation of overviews and specific reports.

WIM is innovative, time efficient and already used in several country-wide inventories.

WIM is a must for every organisation dealing with obsolete pesticide inventories!

Waste Information for Senegal
Selected Waste(s): Dieldrin



INVENTORY AND ASSESSMENT OF OBSOLETE PESTICIDE STOCKS AND EVALUATION OF DISPOSAL CAPACITY FOR HAZARDOUS CHEMICALS IN VIETNAM

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INTRODUCTION

SINTEF and the National Environment Agency (NEA) of Vietnam have carried out the bilateral project "Inventory

and assessment of obsolete pesticide stocks and evaluation of disposal capacity for hazardous chemicals in Vietnam" in the period August 2000 to October 2003. The project was a complementary component of the FAO Programme for Community Integrated Pest Management (IPM) in Vietnam and has been financed by NORAD and partly SINTEF (6:1). Total cost, approximately 300,000 USD.

The project has been performed together with the National Environment Agency (NEA), under the Ministry of Science, Technology and Environment and cooperated with the Obsolete Pesticide Programme of FAO in Rome, FAOs IPM Programme in Vietnam and Vietnam Women's Union Safe Farming Project.

The overall goal of the bilateral project was to raise awareness in Vietnam of the hazards of obsolete pesticides for health and the environment and to prepare the basis for sustainable management of hazardous chemicals in the future.

The objective was that government agencies should perform a nation-wide inventory of obsolete, unwanted and/or banned pesticide stocks. Based on the inventory, the Vietnamese government would have an understanding of the magnitude of the problem and they would know the suitability of their in-country disposal options for hazardous chemicals.

The project contained three main activities:

- Training of Vietnamese authorities in performing a nation-wide inventory according to FAO and UN requirements.
- Evaluation and assessment of the inventory and providing advice regarding site stabilisation and clean up. Providing advice in the implementation of measures to avoid new accumulation of obsolete stocks.
- Evaluation of the disposal capacity for hazardous chemicals in Vietnam and development of a disposal plan.

PESTICIDE USE IN VIETNAM

Vietnam, like other developing countries, faces many pesticide problems. Pesticides have been used in Vietnam since the 1940s and in 1957 pesticide use was reported to be 100 tons per year. By 2002 this has grown to almost 40,000 tons.

The green revolution in rice farming was initiated in the North and South of Viet Nam in the 1960s and plays a significant role in intensive cultivation of rice and other short-seasoned crops. The rice variety IR8 was introduced in the South in 1968 and transformed rice production from extensive farming with a single crop per year to intensive farming with more than 1.4 million hectares of rice-cultivated area in the South by 1988. However, intensive farming is inevitably associated with increased pesticide use and despite the many achievements in pesticide management, farmers still regard pesticides as indispensable. Surveys conducted by the Plant Protection Department in 1992-1997 showed that more than 80% of the farmers considered pesticide application essential compared with other control practices. The pesticides were mainly used against leaf rollers, stem borers, brown plant hoppers, thrips and sheat blight.

Even if Integrated Pest Management" (IPM) has been implemented in Vietnam for many years, government officials admit that the country is one of the largest users of pesticides in the world. The pesticides used are imported as raw materials and manufactured (mixed, reformulated and/or repackaged) in Vietnam. At present, Vietnam has around 60 factories capable of churning out 130,000 tons of agrochemicals per year. Yet, 34,000 tons of such substances were still imported in 2000, not accounting for the amount smuggled via border gates.

Vietnam needs huge amounts of agrochemicals each year to treat more than 10 million hectares of arable land that have already been overexploited. Of the agrochemicals used, pesticides account for 45%, herbicides for 32% and other preventive chemicals for 23%.

Pesticide management covers import, production, formulation, distribution, marketing, training, safe handling and

sound management of obsolete stocks of pesticides. Before 1990, no pesticide management regulations were in place in Viet Nam. With government subsidies, pesticides were imported and distributed to farmers by state agencies. The pesticide use in 1990 was 15,000 tons of finished products, including those in the WHO categories classified to be extremely hazardous. These included Methyl Parathion, Monocrotophos and Methamidophos, as well as the highly persistent DDT and HCH.

A comprehensive nation-wide inspection conducted by the Plant Protection Department in 2002 uncovered:

- 2,388 pesticide retailers operating without a business license (about 23.4 percent of all inspected retailers);
- 5,132 out of 10,233 inspected retailers (50.2 percent) had no store for pesticides, and in many cases, the stores were failing to follow safety regulations (no fire and explosion extinguishers, no first aid kits, and pesticides stored with construction materials, food and animal feeds);
- 2,500 kg of banned pesticides (Methamidophos, DDT and other chemicals);
- 4,753 litres and 5,645 kg of illegally imported or counterfeit pesticides.

In August 2000, a survey of pesticide use among 480 farmers in four provinces in the south considered their confidence, attitude and practices in safe and effective use of pesticides. The survey found that:

- 96.6 percent of farmers use pesticides excessively and not in compliance with the instructions on the labels;
- only 4.8 percent know how to properly dispose of left-over pesticides;
- nearly 95 percent of farmers pour spray remains into canals, ditches or spray on other plants or use it up by continuing to spray;
- 38.1 percent bury pesticide containers and packing after use, most others discard containers in the fields, into the canals, ditches, ponds or sell to scrap collectors or utilize for other purposes.

These reviews highlight some major problems of pesticide management in the country such as: lack of facilities to deal with obsolete and confiscated pesticides; difficulties in export and domestic consumption of vegetables and fruits due to pesticide residues; smuggling of pesticides across the borders; inadequate pesticide stores to meet the environmental safety conditions; small labels with unintelligible print and safety symbols, as well as many other problems.

OBSOLETE PESTICIDES AND POPS IN VIETNAM

There are currently around 100 locations identified with stockpiles of banned and obsolete pesticides in Vietnam. However, most of these stockpiles are mixed pesticides, and it is therefore difficult to identify the POPs component. The Ministry of Agriculture and Rural Development could not quantify the POPs use in the rural areas as there are POPs pesticides being smuggled into (and perhaps out of) the country.

On June 24, 1998 the Minister of Agriculture and Rural Development (Circular No11/1998/TT-BNNPTNT) issued a ban on following POPs pesticides in Vietnam: Aldrin (trade names Aldrite, Aldrex); Chlordane (Chlorotox, Octachlor, Pentachlor), DDT (Neocid, Pentachlorin, Chlorophenothane), Dieldrin (Dioldrex, Dioldrite, Octalox), Endrin Hexadrin), Heptachlor (Drimex, Heptamul, Heptox); Hexachlorobenzene (HCB) (Anticarcin) and Toxaphene Polychlorocamphene). The exception is Mirex, which has probably never been used in Vietnam. The Ministry of Health indicated that DDT importation was banned in 1992 but stockpiles were allowed to clear the system resulting in use termination probably before 1995. Deltamethrin, vecuron, icon, and pyrethroid are now used as substitutes for DDT.

Vietnam does not manufacture or "legally" use any of the POPs pesticide but some reportedly find their way here because Vietnam is a trade route for China and others. The current status of the POPs pesticide use in Vietnam is as follows:

- Aldrin (trade names Aldrite, Aldrex) and Dieldrin (Dioldrex, Dioldrite, and Octalox) are insecticides used to control soil insects. Endrin (Hexadrin) has been used historically as both a rodenticide and an insecticide. All three were referenced in 1991 or 1992 as components of a list of banned pesticides. Use of these three likely continued until such time as all stockpiles were consumed.

- DDT (DDD+DDE) (Neocid, Pentachlorin, Chlorophenothane). DDT came onto the world scene in the early 1940s to control vector-transmitted diseases such as malaria and insects in forestry and agricultural applications. Before 1985, Vietnam used pesticides imported from the former Soviet Union (6,500-9,000 tons per year). Since Vietnam had one of the highest rates of malaria in the world, it has kept data on DDT imports by source (Russia, Netherlands, WHO) and quantities for the years 1957-1990. DDT use went from 315 tons per year in 1961 to 22 tons by 1974 (reductions due to supply cutbacks by the USSR and increasing pest resistance to DDT). Consumption apparently then rose again with consumption for 1962, 1963 and 1981 reported to be at 1,000 tons per year. A paper presented by Vietnam at the 1999 UNEP POPs Workshop states that DDT was banned in 1992, but was still in limited use for "health care" into 1995. (Vietnam reportedly stopped using DDT for Malaria in 1995). According to Ministry of Health, there are likely illegal supplies of DDT currently in use in Vietnam, although DDT has not been used for years for malaria control and nobody reports having it.

- Toxaphene (Polychlorocamphene). Toxaphene, at one time the most heavily used pesticide in the United States,

was banned in the early to mid 1990s in Vietnam. Use likely continued for a short time thereafter until all stockpiles were consumed.

- Heptachlor (Drimex, Heptamul, and Heptox) was referenced in 1991 as a component of a list of banned pesticides. Use likely continued for a short time thereafter until all stockpiles were consumed.

- Mirex has been used as a pesticide primarily targeting fire ants, termites, and other insect pests. It has also been used as a fire retardant agent in plastics, rubber, paint paper and electrical goods. There was no evidence that it was ever imported, manufactured or used in Vietnam. However, as a precautionary measure, it would be wise to ban the import of this chemical.

- Chlordane (Chlorotox, Octachlor, and Pentachlor) was referenced in 1991 as a component of a list of banned pesticides. Use likely continued for a short time thereafter until all stockpiles were consumed.

- Hexachlorobenzene (HCB) (Anticarcin). HCB has been used as a fungicidal seed treatment. It was referenced in 1991 as a component of a list of banned pesticides.

MAIN FINDINGS

β Vietnam has great pesticide consumption due to boosting of the agricultural sector. With an improved economy, it is reasonable to anticipate that the consumption will increase even further.

- After being trained, the Vietnamese authorities carried out a rather complicated nation-wide inventory on their own and mostly financed by own sources. The traditional approach in similar projects has been to solely cooperate with agriculture authorities. In this project, the Vietnam Environmental Protection Agency was chosen as the main counterpart, but in close cooperation with the Ministry of Agriculture and Plant Protection Department. This organisational model has ensured broad awareness-raising and stimulated inter-departmental cooperation.

- More than 10,000 tons of dioxin-contaminated soil, more than 225 tons of 200 different pesticides and 1.7 million containers are currently accumulated in more than 100 locations.

- The accumulated amounts identified by the inventory seem to be reasonable and comparable with inventories from other countries.

- Most of the stockpiled obsolete pesticides are stored under relatively good conditions.

- Vietnam has a huge contaminated soil problem and this needs to be solved in a cost-efficient and sound way.

- By August 2003, many of the Provinces have already disposed of their identified stocks, mainly by hiring the Ministry of Defence's mobile incinerator.

- Smuggling is already a serious problem and should be given attention.

- The feasibility study of disposal options uncovered a need of environmentally sound treatment options in Vietnam.

- Vietnam has signed and ratified the Stockholm Convention on POPs and initiated the development of a National Implementation Plan.

SUMMARY

OF SESSION ON WASTE: DESTRUCTION TECHNIQUES

Leon Urlings and Stanislaw Stobiecki

New system: water treatment CIHC, As	Bioadsorber= arable raw material High concentration factor. (Better than Active Carbon)
Cement Kiln	1500 C 20 ton/2days 2-6% A.I., 11-30% liquid waste in fuel < detection limit Condition needed. Monitoring/take care Fuel mix Adm. decision took 2 year
Hydrodechlorination (metal catalysts)	50 C, No H ₂ , P=1 atm Optimal catalyst in multiphase
Gas Phase Chemical Reduction (Eco Logic)	850 C 6300 ton/7year 99.9999%
NEFCO (Multilateral Financial Inst.) 5 Nordic Countries	Project requirements fin./regulation PCB transformers 1200 C 99.9999 3800 Euro/ton
BCD Base Cat. De-Chlorination	350 C >100.000 ton Now implemented at Spolana
POP elimination CEE	DANCEE study BCD costly low capacity: Remark 150t/month Cement Kiln less sustainable CEE after 2004 EU-legislation/ different Phases/ split up region, different requirements
Latvia Progress	2001- now, no change at al (start '99) NIMBY Danish Incinerator, 300kg/h Adm. decision, EIA, no decision after serious delay, 2nd part 2003
Best technique, good or bad	No off the shelf technology Cost per ton is not only driver Public acceptance
To incinerate or not to incinerate	
Role of government	Able to judge technology and effect on public acceptance
Coping with uncertainties	Technology is solid and stable. Can help in acceptance

A NEW HCH-DECONTAMINATION TECHNOLOGY (PAT.PEND.): BASICS AND APPLICATION

Günther Mann

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ABSTRACT

It is long-known that long lasting application of pesticides, especially HCH (Lindane), caused remarkable damages to environment and endangers human and wildlife health. Following a new technology for the decontamination of liquids containing HCH is described. Furthermore a modular system is introduced which is operating on the basis of this new technology and can be used for various types of contamination.

PROBLEM AND STATE OF ART

HCH (1,2,3,4,5,6 hexachlorocyclohexane), is known as a reaction product of benzene and chlorine and occurs in 8 stereo-isomers. Five of those isomers are of technical importance, especially the gamma-isomer which is known as Lindane for its insecticidal properties. Lindane has been used worldwide with almost no restrictions for many years.

Only in the last years the resulting dangers for health and environment have been examined and registered, accompanied by efforts to develop and apply suitable technical decontamination procedures for the expedition of the relatively slow natural decomposition (by microorganisms and sun light). These technologies work on classic thermal, biological or chemo-physical principles but often provide a number of disadvantages such as:

- high expenses, high energy consumption, large time factor,
- formation of undesirable secondary products.

A NEW AND BETTER SOLUTION:

THE MENEX®™ - BIOADSORBERS

Throughout the last 7 years in co-operation with the Fraunhofer Institute for Interfacial Engineering and Biotechnology in Stuttgart (Germany) a series of adsorbers and/or ion exchangers were developed based on arable raw material and called Menex®™- Bioadsorbers (2). The main aim is using natural adsorbing and ion-exchanging processes for technical purification procedures of contaminated liquids. A slight modification in the production process of these bioadsorbers enables their application in various fields as follows:

- Purification of heavy metal contaminated media,
- Purification of radioactive contaminated media,
- Purification of media, contaminated with different types of chlorinated hydrocarbons (3-5)

During 2001, efficiency of using these adsorbers in HCH decontamination was proved. In that case, the menex®™ - bioadsorbers type KLX produced on the basis of wheat bran were capable to reduce the HCH contents in real seepage water. Levels of decontamination achieved reached the same as in the case of using continuous (fixing KLX in columns) as well as in batch procedures. The decontamination factor reached >10 in all cases where the initial HCH concentration was within ppb range.

Decontamination "Modern" plant, a modular and mobile system for removal of HCH and As

The task was decontamination of HCH and As containing liquids to statutory limit values. The initial concentrations of HCH and As recorded <20 ug/l and < 3,000 ug/l respectively. A limit value of < 1 ug/l HCH and < 50 ug/l As had to be reached at a flow rate of 50 to 100 l liquid per hour. On the basis of the a.m. tests, an applicable technology was developed, manufactured and applied in the respective plant.

After various optimization steps of the technology, the plant comprise the following components (pat.pend.):

- Module 1: modified electro flotation in quasicontinuous operation and settling tank
- Module 2: sand filter unit
- Module 3-5: menex®™ - filter units
- Module 6: filter unit for post removal of As (granulated iron hydroxide)
- Module 7: activated carbon filter unit
- removal of filtrate and disposal of sludges
- electronic control and monitoring system.

Each and every single module can be connected/disconnected according to the contents of the raw water. In automatic operation of the plant an exchange/regeneration of the filter modules is only necessary after 150 operation hours or 7.5 m₃ raw water. Investment and operation costs are far below those of other systems as mentioned previously (state of the art). The following decontamination levels were achieved:

HCH input:	1.1.....20ug/l
HCH output:	0.05....0.9 ug/l
(given value limit: 1ug/l)	
As input:	2.....3,600 ug/l
As output:	1.....11 ug/l
(given value limit: 50 ug/l)	

Furthermore the values for AOX and COD could be reduced essentially.



Figure 1. Menex®™ - Bioadsorber, Type KLX

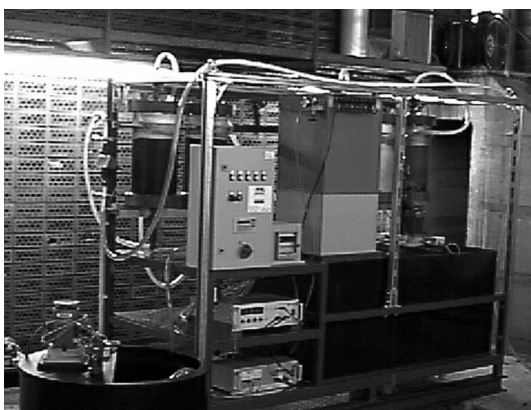


Figure 2. „Modern” System Used by a Customer
(plant without cover)

DISPOSAL OF OBSOLETE PESTICIDES AS AN ALTERNATIVE FUEL IN CEMENT KILN

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SUMMARY

The disposal of obsolete pesticides wastes collected and accumulated in the last 50 years is a serious ecological problem, which requires a systemic solution. The disposal methods should be selected in such a way that they complement one another and the owner or holder of obsolete pesticide stock would be able to choose the most appropriate disposal method in each given case. The criteria for the disposal method selection should take into account the hygienic, toxicological, environmental and economic aspects. The main goal of the present project was to create bases for a technical scale utilization of pesticides as an alternative fuel ingredient in the production of clinker in a cement kiln. The method is recommended for selected pesticides with known compositions. The project covered all aspects of the issue: selection, delivery and separation of wastes intended for disposal as an additive to fuel based on light heating oil, developing recipes, assembling a technological line for fuel production, fuel manufacturing, fuel analyses, co-burning fuel with fine coal during clinker production, comprehensive sampling and monitoring the disposal process at the cement plant. A crucial part of the project was to obtain administrative permits allowing for the

Literature

- (1) Roempp Lexikon Chemie, 10th edition, version 2.0, Georg Thieme Publishers, Stuttgart
- (2) „Heavy metal adsorbents from renewable resources“, Information sheets of the Fraunhofer Institute for Interfacial Engineering and Biotechnology, Stuttgart, 2002
- (3) „Kleie filtert Chlorkohlenwasserstoffe und Arsen aus Abwässern“, press release of the Fraunhofer Institute for Interfacial Engineering and Biotechnology, Stuttgart, 10 October, 2002
- (4) „Arsen in aller Munde“, Chemische Rundschau, 25 February, 2003
- (5) „Bioadsorber für die Schadstoff-Eliminierung“, Scope, 11 March, 2003

production and utilization of alternative fuel with added pesticides. The permits themselves required a number of auxiliary studies and documents. The formal and legal procedures were very lengthy and the decision to allow for further studies depended on the positive results of the first experiment.

Three alternative fuel recipes were developed with 11 active ingredients of pesticides and three batches on technical scale were produced. Co-burning of that fuel with fine coal was a subject of experimental sessions. Full monitoring of the whole process was carried out. The levels of dioxins, furans in exhaust gases were below the standards. No changes in the quality of the products were observed also.

PROJECT OBJECTIVES AND TASKS

The project was performed as an European Union's PHARE project

No. PL 9608-01-02-03: „Pilot project of utilizing obsolete pesticides as alternative fuel in cement kiln”.

The project consists of eight major tasks:

- | | |
|----------------|--|
| TASK 1: | Sorting and preparation of wastes |
| TASK 2: | Wastes transport |
| TASK 3: | Wastes analysis |
| TASK 4: | Technology development |
| TASK 5: | Supervising the process of alternative fuel production |
| TASK 6: | Analysis of the output fuel |
| TASK 7: | Waste disposal management |
| TASK 8: | Measurement of the disposal process |

Following the above tasks, collaboration with Chemical Works „Organika-Azot” S.A. and Cement Plant Rejowiec S.A. according to the agreement of February 29th, 2000 is crucial to the project that relies on proper coordination of both technical and logistic activities. Producing alternative fuel based on light heating of oil with the addition of liquid pesticidal wastes is a difficult and unique task undertaken in Poland for the first time. World literature and reference materials are rather scarce with respect to this process (Schimpf 1998, Karstensen 2001). Great attention must

also be given to the legal aspects of the experiment. Multiple tasks within the project make it organizationally complex, which is not subject to detailed reporting.

The objective of the project is to create basis for future technical, organizational and legal actions aiming at utilizing the alternative fuel containing pesticides at a technical scale in the process of manufacturing cement in cement kilns.

The first stage of the project was reported at 6th International HCH and Pesticides Forum in Poznań (Stobiecki 2001).

ALTERNATIVE FUEL COMPOSITION

The project resulted in the development of three different alternative fuel recipes. The total amount of the biologically active ingredients of pesticides does not exceed 10%. The components for each type of fuel were empirically selected for small-scale laboratory production. Components must be combined so as the outcome fuel has appropriate physical and chemical properties and stability. After obtaining satisfactory parameters, large-scale laboratory batch is produced in the amount of about 20 kilograms and this batch is then subjected to a comprehensive testing. The right recipe is crucial for the overall success of the project. Following are the three recipes:

Recipe 1

Contains 8 active pesticidal ingredients: methoxychlor, gamma-HCH, alpha-HCH, fenitrothion, fention, pp' DDT, endosulfan, p-dichlorobenzene.

Sum of active ingredients was 2.238%.

Recipe 2

Contains 8 active pesticidal ingredients: methoxychlor, DNOK, pp' DDT, endosulfan, gamma-HCH, alpha-HCH, p-dichlorobenzene, esfenwalerat.

Sum of active ingredients was 5.960%

Recipe 3

Contains 11 active pesticidal ingredients: metoxychlor, fenitrothion, DNOK, gamma-HCH, alpha-HCH, pp' DDT, carbosulfan, deltamethrine, endosulfan, p-dichlorobenzene, esfenwalerat.

Sum of active ingredients was 7.021%

Table 1 shows the summary of the contents of three recipes.

Fuel Recipe No.	Heating value in kJ/kg	Combined a.i. contents %	Combined pesticide contents – formulations %
1	44545	2.238	11.48
2	43193	5.905	29.38
3	42968	6.396	30.48

Table 1: Summary of recipe properties

WASTE DISPOSAL IN CEMENT KILN

The fuel was produced at the Chemical Plant “Organika-Azot” in Jaworzno. Three batches were manufactured: Recipe No 1: 10 tons, Recipe No 2: 5 tons and Recipe No 3: 5 tons.

The fuel batches were transported immediately after manufacturing by a tanker to the Cement Plant in Rejowiec. Co-burning with the fine coal was the most important part of the experiments. The prototype burner was placed next to the cement kiln intake and connected through fuel lines to a tanker located at a safe distance, behind a cement wall of technological halls. For the duration of the experiment, the burner was operated by the employees of the Mineral Building Materials Institute, accompanied by two fireman units (the company's and a special unit from Chełm) and the Special Pesticide Emergency Team from the Plant Protection Institute with 5 chemical guards. The Cement Plant and the Plant Protection Institute throughout the whole experiment provided technical supervision. The process of burning Recipe 1 alternative fuel in kiln No.4 began on 28.06.2001 at 12:00 noon and ended on 29.06.2001 at 12:00 noon. The trial to co-burn alternative fuel with fine coal was very successful. No emergencies occurred and the process proceeded stable. Safety precautions were taken. The key trial of 28.06.2001 was preceded by an experiment of co-burning light heating oil only on 26.06.2001. The outcome was successful. Recipes 2 and 3 fuels were incinerated on 23-24.10.2002. Similarly, it was a very stable operation. No emergencies occurred and safety precautions were taken.

MONITORING

Monitoring the experiments with the alternative fuel was the key element of the entire project. A full and complete monitoring covered the whole system, including fuel; exhaust gases, the outcome product and ashes. Following the decisions of the Provincial Office in Lublin, the monitoring procedures were consulted with the Provincial Environmental Protection Inspection in Lublin. Analyses were carried out at the following special labs:

1) Politechnika Krakowska – EMIPRO Sp. z o.o. Kraków [Cracow Polytechnics]– sampling and analyses with regards to emissions from the experiment.

2) Instytut Mineralnych Materiałów Budowlanych Oddział w Krakowie [Mineral Building Materials Institute, Cracow Branch] – physical properties and quality of outcome product.

3) Politechnika Śląska [Silesian Polytechnics]– analyses of alternative fuel properties.

4) Instytut Ochrony Roślin Oddział Sosnowice [Plant Protection Institute]– pesticide bioactive ingredient determinations.

RESULTS

The results of analyses were placed in detailed Annexes in the Final Report of the project. As an example Tables 2 and 3 include the trace determinations for pesticides in exhaust gases and clinkers produced with co-burnt alternative fuel.

No.	Name of a biologically active ingredient	Detection limit ug/m3	Exhaust gases Recipe 1 28.06.2001	Exhaust gases Recipe 2 23.10.2002	Exhaust gases Recipe 3 24.10.2002
1.	DDT (combined isomers)	0.05 – 0.20	nd	nd	nd
2.	Gamma-HCH	0.02	nd	nd	nd
3.	Alpha-HCH (+ other isomers)	0.02 – 0.10	nd	nd	nd
4.	metoxychlor	0.3 – 0.5	nd	nd	nd
5.	fenitroton	0.05 – 0.15	nd	nd	nd
6.	fention	0.05 – 0.15	nd	nd	nd
7.	endosulfan	0.05 – 0.20	nd	nd	nd
8.	p-dichlorobenzene	0.15	nd	–	–
9.	esfenwalerat	1.0	–	nd	nd
10.	DNOK	1.0	–	nd	nd
11.	deltametrine	0.5	–	nd	nd
12.	carbosulfan	1.0	–	nd	nd

nd = not determined

Table 2: Results of trace determinations for pesticides in exhaust gases.

No.	Name of a biologically active ingredient	Detection limit ug/m3	Clinker Recipe 1 28.06.2001	Clinker Recipe 2 23.10.2002	Clinker Recipe 3 24.10.2002
1.	DDT (combined isomers)	0.001 – 0.005	nd	nd	nd
2.	Gamma-HCH	0.001	nd	nd	nd
3.	Alpha-HCH (+ other isomers)	0.001 – 0.002	nd	nd	nd
4.	Metoxychlor	0.005 – 0.020	nd	nd	nd
5.	fenitroton	0.001 – 0.005	nd	nd	nd
6.	fention	0.001 – 0.005	nd	nd	nd
7.	endosulfan	0.002 – 0.005	nd	nd	nd
8.	p-dichlorobenzene	0.050	nd	–	–
9.	Esfenwalerat	0.010	–	nd	nd
10.	DNOK	0.020	–	nd	nd
11.	deltametrine	0.010	–	nd	nd
12.	carbosulfan	0.025	–	nd	nd

nd = not determined

Table 3: Results of trace determinations for pesticides in clinkers.

CONCLUSIONS

The process of co-feeding alternative fuel with fine coal during clinker production was comprehensively sampled. The full and complete monitoring approach relied on selecting all elements of the system necessary to undergo analyses and determination the scope of the analyses for each element. The experiment had three sampling sessions for Recipe 1, 2 and 3 alternative fuel batches and a background session covering the regular operational conditions during clinker production. Exhaust gases were tested for volatile organic compounds, toxic metals, HCl, HF, inorganic gases, volatile dust, total inorganic coal and polychlorinated dibenzodioxines and dibenzofuranes. The reports from the four sessions of exhaust gases sampling

done by EMIPRO Kraków included a detailed description of the results and a full analytic documentation. The results of determinations for concentrations of dioxines and furans PCDDs and PCDFs are as follows:

- 1) Background (27.06.2002) – 0.009 ng TEQ/m³n
- 2) Session with fuel– Recipe 1 (28.06.2001) – 0.015 ngTEQ/m³n
- 3) Session with fuel– Recipe 2 (23.10.2002) – 0.053 ngTEQ/m³n
- 4) Session with fuel– Recipe 3 (24.10.2002) – 0.068 ngTEQ/m³n

The results of determinations for dioxins and furans as per the four sampling sessions are lower than admissible levels as described in EU Directive 2000/76/EC and Polish

regulations (admissible concentrations below 0.1 ngTEQ/m³n), it should be noted, however, that with alternative fuel feed an increase in chlorine content in alternative fuel causes an increase of dioxins and furans in exhaust gases from 0.009 ngTEQ/m³n (background trial, no alternative fuel) to 0.068 ngTEQ/m³n (with maximum chlorine content in alternative fuel).

Other results did not indicate any major differences between the concentrations of the substances in exhaust gases from background sampling session as compared with the fuel sessions.

Determinations carried out by the Plant Protection Institute on exhaust gas extracts indicated that pesticide biologically active ingredients were fully broken down. No pesticide residues were found in exhaust gases.

The Institute of Mineral Building Materials in Cracow analyzed materials sampled during the four sessions. Sludge, clinker, ashes and dusts, including heavy metal content analyses and studies of heavy metal elution from clinker and cement, as well as testing physical and mechanical properties of cement were performed. The results indicate that admixing the alternative fuel had no impact on the production process and the quality of produced cement. Physical and mechanical properties of clinker and cement produced with co-fed alternative fuel are very similar to

those from a routine production process. The heavy metals content and the elution levels are also similar.

The process of co-feeding of alternative fuel containing pesticides with fine coal during clinker production is a good method for pesticides disposal. The detailed monitoring of all elements of the experimental system showed no effect on the exhaust gases.

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HYDRODECHLORINATION OF POLYCHLORINATED ORGANICS OVER SUPPORTED CATALYSTS AND RANEY-NI UNDER MULTIPHASE CONDITIONS

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ABSTRACT

Dechlorination of lindane, dieldrin, 2,4,5-trichlorophenoxyacetic acid, and of some other POPs, proceeds rapidly in a multiphase catalytic system, composed by isooctane and aqueous KOH phases, a phase transfer agent (Aliquat 336) and a metal catalyst, e.g. 5% Pd/C, 5% Pt/C, or Raney-Ni. In most cases the complete dechlorination of polychlorinated substrates and their quantitative conversion to the innocuous hydrocarbons is achievable at only 50 °C and atmospheric pressure of hydrogen in very short reaction times. The presence of aqueous KOH and of a promoter, Aliquat 336, in the system is shown to have a decisive role not only in promoting hydrodechlorination but also in producing the selectivity changes of the reaction. The opti-

mised reaction conditions (e.g. system composition, catalysts, etc.) for dechlorination of particular substrates, selectivity features, and mechanistic considerations on the mode of action of multiphase environment in the hydrodechlorination reaction are discussed.

INTRODUCTION

The catalytic hydrogenolysis of organochlorine compounds (hydrodechlorination, HDC) is a viable, low-cost, and green methodology with a potential to be employed for degradation of the hazardous polychlorinated aromatics and aliphatics, such as polychlorinated benzenes, chlorophenols, halogenated C1-C3 hydrocarbons, PCBs, pesticides, and dioxins. The HDC reaction in the liquid [] and gas phase [] is being intensively studied nowadays.

As a rule, supported palladium is reported to be the most active catalyst; however there are examples of using supported Ni catalysts, and some other metals, as well []. Since the HDC process is usually connected, especially in the gaseous systems, with harsh reaction conditions (high temperatures and/or pressures) there is a need to develop stable and active catalysts, resistant to deactivation, which is usually an issue if high temperatures are involved. Alternatively, research can proceed to identify novel systems to carry out the reaction under milder conditions. The use of liquid phase systems partially solves this problem. However, certain solutions are required to render the liquid phase systems efficient operating with hydrogen gas; certain hydrogen donors, e.g. formates, afford easier reduction

but are costly with respect to hydrogen gas. Catalyst deactivation can be avoided if the hydrochloric acid produced in this reaction is eliminated from the system. The gas phase systems, even though more practically advantageous than the liquid phase ones, because they operate continuous flow, usually suffer from the presence of HCl, whilst the liquid phase systems can be introduced with alkali (the traditional liquid phase HDC systems employ alcoholic alkali solutions as reaction media).

The multiphase system is a solution for HDC; it is based on the liquid phase methodology, where the alkali (usually KOH) is present in a separate aqueous liquid layer, and a polychlorinated substrate is present in a hydrocarbon solvent (usually isooctane). The separation of reagent and alkali is advantageous since it makes it easier to recover the reaction products, but needs a promoter to bring the alkali and the reagents to the catalyst surface. This promoter was found to be a quaternary ammonium salt, e.g. the commercially available and widely used in phase-transfer catalysis Aliquat 336. Surprisingly, it turned out that its presence not only makes the reaction possible and with no sensible sign of catalyst deactivation (normally the reaction simply does not proceed in a biphasic aqueous organic system without quaternary salt), but also renders the HDC process faster than in alcoholic base systems. The role of Aliquat 336 as of the promoter in this system is intriguing also because it opens up possibilities to vary the reaction selectivity and to use catalysts, which seemed to be almost inactive in this reaction (e.g. the use of non-expensive Raney-Ni in dechlorination of polychlorinated substrates).

Herein we overview some of our recent results and report some new data on the use of commercial Pd/C, Pt/C and Raney-Ni in the multiphase HDC of some toxic polychlorinated aromatics and aliphatics. It is now of worldwide importance that the stockpiles of toxic substances like lindane, which is a heavily used insecticide with possible carcinogenic effects and which appears on the CERCLA Priority List of Hazardous Substances, as well as other pesticides, like dieldrin, DDT, 2,4,5-T, etc. and PCBs which

are on the UNEP's POP list, be transformed into innocuous substances, or be destroyed in order to satisfy the requirements of the Stockholm convention on POPs.

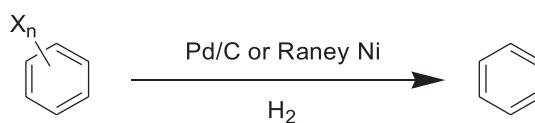
EXPERIMENTAL

A 25-ml three-necked round-bottomed flask thermostated at 50 °C, connected to a system for the addition of hydrogen and with a water-jacketed condenser, was employed for the reaction. If not otherwise indicated a 10 ml isooctane (or isooctane-toluene) solution of a chlorinated substrate (0.7 mmol) and Aliquat 336® (0.103 g, 0.26 mmol), containing a suspension of 5% Pd/C or 5% Pt/C (0.021 mmol of metal) or 50% aqueous Raney-Ni slurry (0.25 g, 2 mmol of Ni) were placed into the reactor together with 5.7 ml of aqueous base solution. In case if the reaction was carried in EtOH or EtOH-water, 10 ml total solution volume was used for the reaction. The mixture was then stirred magnetically at 1000 rpm and bubbled with hydrogen at approximately 10 ml/min. Samples of the reaction mixture were collected periodically, and analyzed by means of GC, GC-MS, or HPLC.

RESULTS AND DISCUSSION

Different isomers of polychlorobenzenes (from mono- to tetra) and other halogenated benzenes (iodinated and brominated) have been shown to undergo effective hydrodehalogenation over Pd/C or Raney-Ni with hydrogen under multiphase conditions [].

From the data presented in Table 1 on the HDC of 1,2,4,5-tetrachlorobenzene one can see that the reaction requires a base in the aqueous phase to eliminate the HCl formed and thereby retain the catalytic activity, but the highest rate is obtained when base and Aliquat 336 are present together in the system. The final product, benzene, is formed in quantitative yields and no other products, e.g. arising from the coupling reaction or ring hydrogenation were detected in sensible amounts. The presence of Aliquat 336 was found to particularly enhance the dechlorination rates of polychlorinated benzenes and of sterically hindered chlorines, e.g. in chloroxylenes, etc.



Scheme 1

Aqueous phase	Aliquat 336	Time, min	Conversion, %	Yields % (GC)			
				TCB	DCBs	PhCl	PhH
no	no	120	29	16	5	–	–
KOH (50%)	no	30	100	4	19	4	73
KOH (50%)	yes	30	100	–	4	–	96

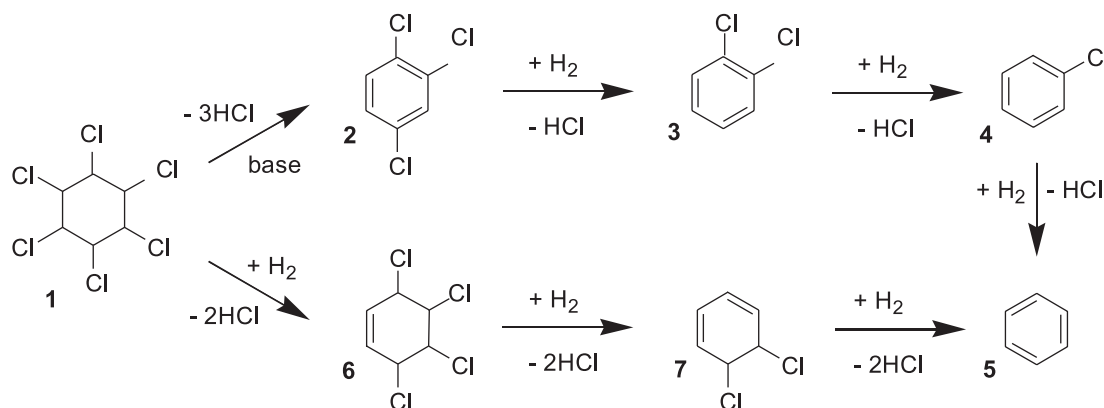
Table 1: HDC of 1,2,4,5-tetrachlorobenzene over Pd/C 5%

The effect of Aliquat 336 is especially pronounced in the HDC of polychloroaromatics over Raney-Ni []. For example, the HDC of 1,3,5-TCB over Raney-Ni proceeds only if the base and Aliquat 336 are simultaneously present in the system, and not if one of these is missing. The concentrations of aqueous base, such as KOH, carbonates or bicarbonates, between 4 and 10% are optimal, whereas more concentrated base has a deactivating effect.

The mode of action of the quaternary salt in the system is not completely understood, but is unequivocally con-

nected to the adsorption of the quaternary salt on the catalyst surface, which has been proven kinetically for the reactions of chlorinated benzenes over Pd/C and Raney-Ni [5, 6].

Not only reduction of aromatic compounds benefits from the multiphase environment, i.e. the presence of Aliquat 336 in the biphasic organic – basic aqueous medium. Polychlorinated aliphatic substrates, such as lindane (gamma-hexachlorocyclohexane) (see Scheme 2) and diel-drin (Scheme 3) do also undergo dechlorination.



Scheme 2

Dechlorination of lindane (**1**) in the multiphase system [], with the catalysts such as 5% Pd/C, 5% Pt/C, or Raney-Ni (Table 2) proceeds rapidly (in 5–10 min) to 1,2,4-trichlorobenzene (**2**) via the base-assisted dehydrochlorination (DHC), followed then by three consecutive steps of catalytic HDC with hydrogen to benzene (**5**).

Catalyst	Time, min	Conversion, %	Yield, % (GC)			
			2	3	4	5
5% Pd/C	7	93	35	25	25	6
	22	100	26	10	6	48
	190		0	3	6	91
Raney-Ni	5	100	94	4	0	2
	90		1	3	0	96
5% Pt/C	5	100	75	19	2	4
	250		10	65	12	13

Table 2: Reaction of lindane with H₂ over metal catalysts in the isooctane–7% aqueous KOH system in the presence of Aliquat 336

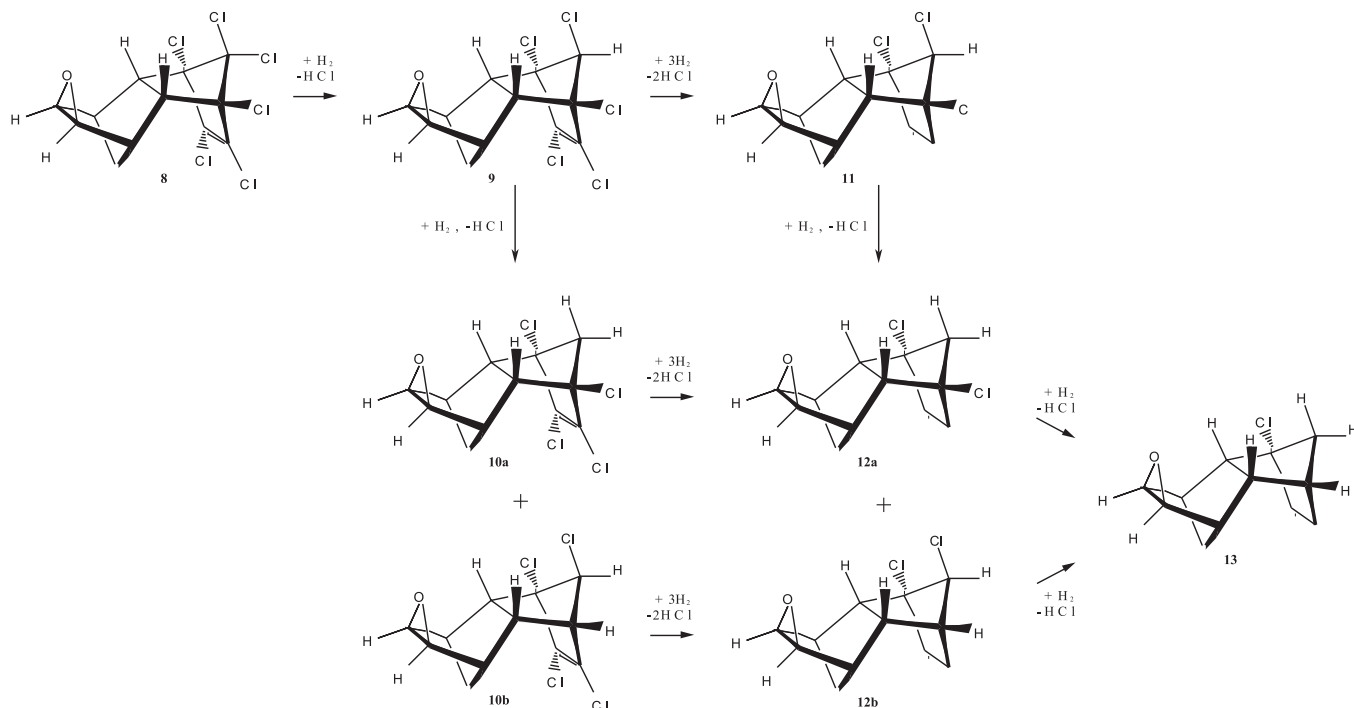
Catalyst	Time, min	Conversion, %	Yield, % (GC)			
			6	7	other*	5
5% Pd/C	50	100	0	0	3	97
	280		0	0		100
Raney-Ni	30	40	0	0	5	35
	270	99	0	0	2	97
5% Pt/C	10	93	25	12	15	41
	20	100	0	0	15	85

Table 3: Reaction of lindane with H₂ over metal catalysts in the isooctane–water system in the presence of Aliquat 336

* **3**, **4**, pentachlorocyclohexane, pentachlorocyclohexene, chloro- and dichlorocyclohexanes

Aqueous KOH and Aliquat 336 strongly affect the reaction: if present together they promote both the DHC (where Aliquat 336 acts as a phase-transfer catalyst) and the HDC steps; if KOH is absent, the reaction has been found to follow a different catalytic pathway, which involves a removal of a pair of adjacent chlorines at every reaction step by zerovalent metal followed by reduction of metal with hydrogen. This is proven by the formation of 3,4,5,6-tetrachlorocyclohex-1-ene (**6**) and

5,6-dichlorocyclohexa-1,3-diene (**7**) as intermediates in the reaction over Raney-Ni, and by the absence of even a trace of trichlorobenzenes in the reaction mixture (see Table 3). The full conversion to benzene via this alternative pathway is achieved in shorter times than in the system with KOH. Also in this case (in the isooctane-water system), the presence of Aliquat 336 produces nearly a 10-fold rate increase, and the presence of the aqueous phase, even if neutral, is indispensable, since the latter seems to scavenge HCl, thereby preventing inhibition.



Scheme 3

In the reaction of dieldrin (see Scheme 3) over Pd/C or Raney-Ni in the multiphase system or in the ethanolic base solution, the full conversion of starting material occurs rapidly (10-20 min) with a high selectivity towards the mono-dechlorination product **9** (up to 80%, structure confirmed by NMR); the following HDC steps are significantly slower (see Table 4). In the end, the reaction over Pd/C can give a mixture of products **9**, **10**, **11**, **12**, **13**, and where less selective, but deeper reduction (up to the elimination of 5 chlorines) was observed in the presence of concentrated KOH or in the ethanolic KOH system (the suggested pathway in this case involves all the steps of Scheme 3). The general pathway of the reaction on Pd/C in the multiphase system with diluted base follows the **8-9-11-12a** sequence (Scheme 1). After the removal of the first chlorine in **8** the next step involves a concerted removal of two chlorines at the double bond

and hydrogenation of the latter, giving right away **11**. Normally, the removal of the second CC12 bridge chlorine in **11** to **12a** occurs only afterwards. In the ethanolic system or in the system with concentrated base, the reduction of the chlorine atom at bridgehead carbon in **8** took place, as well.

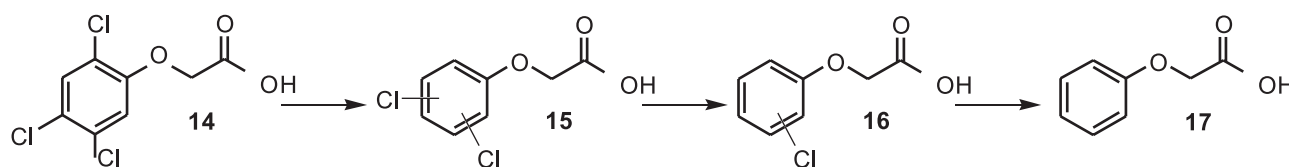
On the contrary, the reaction over Raney-Ni, the chlorine atoms at bridgehead carbons, which are poorly reactive on Pd/C, appear to be fairly reactive, whilst the chlorines at the double bond, instead, do not reduce. The reduction of **8** over Raney-Ni proceeds via the **8-9-12b** pathway and can be conducted selectively to **12b** (86% yield, structure confirmed by NMR). The reaction in the absence of Aliquat 336 is slow on Pd/C and does not proceed at all on Raney-Ni. Furthermore, the reaction on Raney-Ni is inhibited if carried out in the ethanol medium (Table 4).

Catalyst	Solvent	Aliquat 336	Time, min	Conversion, %	Yield, % (GC)				
					9	10	11	12	13
Pd/C 5%	<i>i</i> -octane toluene*	yes	14	100	80	0	8	12	0
			380		32	0	52	16	0
Pd/C 5%	<i>i</i> -octane toluene*	no	141	74	60	0	12	2	0
			230	100	76	0	20	4	0
			430		55	0	37	8	0
Pd/C 5%	EtOH	no	10	97	79	5	8	5	0
			195	100	29	9	31	25	6
Raney-Ni	<i>i</i> -octane toluene*	yes	150	100	87	13	0	0	0
			1000		6	86	0	0	0
Raney-Ni	EtOH	no	330	1	1	0	0	0	0

Table 4: Hydrodechlorination of dieldrin over 5% Pd/C and Raney-Ni in different solvent systems with KOH (7% aqueous or ethanolic).

HDC of 2,4,5-trichlorophenoxyacetic acid (**14**) over Pd/C and Raney-Ni in the biphasic aqueous – organic or the ethanol – aqueous media in the presence of KOH proceeds via three consecutive dechlorination steps, giving the fully dechlorinated acid (**17**) and/or the corresponding potassium salt, as shown in Scheme 4. It has been found that the presence of Aliquat 336 in the biphasic aqueous – isooctane

system allows increasing substantially the solubility of the acid (present predominantly in the organic phase in this case), probably because of the formation of an ionic pair of the acid anion with the quaternary cation of Aliquat 336. However, the better reaction rates are observed in an aqueous-ethanolic (1:1 vv) basic medium, where both acid and its salt are well soluble.



Scheme 4

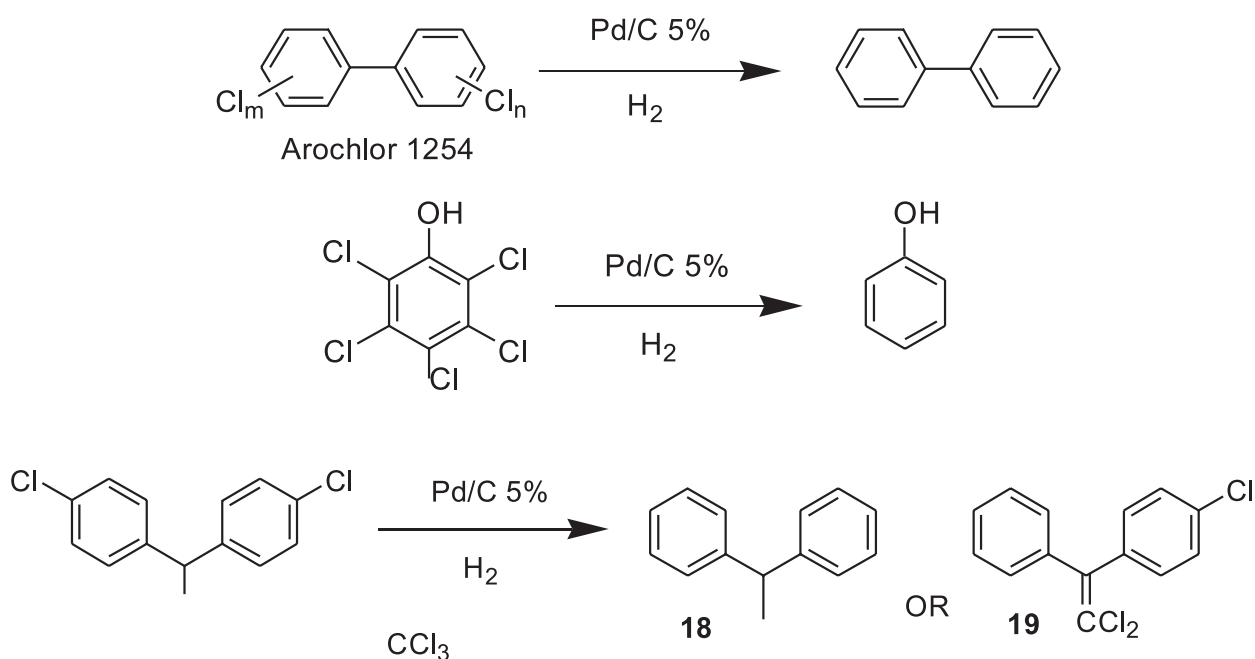
Catalyst	Solvent	KOH, %	A336	Time, min	Conv., %	Yield, % (HPLC)		
						15	16	17
5% Pd/C	<i>i</i> -octane	2 aq.	yes	210	99	1	4	89
Raney-Ni	<i>i</i> -octane	2 aq.	yes	210	84	5	5	74
5% Pd/C	EtOH-H ₂ O	7	no	73	100	0	0	99
Raney-Ni	EtOH-H ₂ O	7	no	230	100	0	0	98
5% Pd/C	EtOH-H ₂ O	7	yes	150	100	5	48	47

* 0.07 M if in EtOH-H₂O and 0.007 M if in isooctane

Table 5: Hydrodechlorination of 2,4,5-*T** with hydrogen over 5% Pd/C and Raney-Ni

Other toxicants, such as polychlorinated biphenyls (PCB), pentachlorophenol (PCP), and DDT have been also shown to undergo complete reduction with hydrogen in a system with Pd/C 5%, concentrated KOH, and Aliquat 336 (Scheme 5). The reactions of PCB and PCP are complete in 3 and 5 hrs with the yields of 99% and 96%, respectively. In the absence of A336 the corresponding yields are

achieved in 5 and 8 hrs respectively, i.e. the reactions are nearly twice as slower. DDT gives 100% of the full dechlorination product 1,1-diphenylethane (**18**) in 9 hrs in the multiphase system, whilst in the same system without Aliquat 336 the reaction (run for 8 hrs) affords only 3% of **1** and the products of partial dechlorination, of which 75% is **19** (see Scheme 5).



Scheme 5

In conclusion, it has been demonstrated by a number of examples that the proposed multiphase method is very efficient for the HDC reaction of organochlorine toxicants and thereby represents an alternative solution to the existing technologies for waste treatment, because 1) it is based on reduction, i.e. the possibility of formation of more toxic by-products is excluded, 2) it is catalytic, i.e. less energy consuming, 3) it is viable and safe, i.e. operating at mild conditions, and 4) first and foremost, it is an utilisation approach, i.e. useful chemicals can be produced out of polychlorinated waste. Research is now being run to improve the reaction conditions by introducing alternative promoters, hydrogen donors, and solvent systems, as well as to understand the mechanistic role of the multiphase environment in promoting hydrogenolysis of organic chlorine.

ACKNOWLEDGEMENTS

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PCB WASTE TREATMENT IN THE SLOVAK REPUBLIC USING GAS-PHASE CHEMICAL REDUCTION

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ABSTRACT

Gas-Phase Chemical Reduction (GPCR) is a non-incineration technology developed by Eco Logic of Ontario, Canada. GPCR involves the reduction of organic compounds (such as PCBs and pesticides) by hydrogen at temperatures of 850°C or greater. Organic compounds are ultimately reduced to methane, hydrogen chloride (if the waste is chlorinated), and minor amounts of low molecular weight hydrocarbons (benzene and ethylene). The hydrochloric acid is neutralized by addition of caustic soda during initial cooling of the process gas. The ability of GPCR to destroy organic contaminants with efficiencies in excess of 99.9999% has been proven numerous times in demonstration tests and commercial-scale operations. Suitable waste matrices include liquids, high-strength oils and solid materials. GPCR has been used to treat thousands of tonnes of hazardous organic compounds since 1995, and to date over 30,000 operating hours have been logged with the technology at sites worldwide.

Recently the GPCR technology was selected for the treatment of PCB-contaminated material at an industrial site in the Slovak Republic, under a pilot project with the United Nations Industrial Development Organisation (UNIDO). The GPCR plant will be used to treat PCB wastes that are currently located at the industrial facility, as

well as wastes that are brought in from other locations throughout the Slovak Republic.

The presentation will describe the GPCR technology, including its waste feed systems, reaction chemistry and output handling and recovery, its status worldwide, and its application to the UNIDO project in Slovakia.

INTRODUCTION

Gas-Phase chemical Reduction (GPCR) is a non-incineration hazardous waste treatment technology developed by ELI Eco Logic International Incorporated (Eco Logic) of Rockwood, Ontario, Canada. The technology has been patented and proven for treatment of hazardous organic compounds such as PCBs, pesticides and other Persistent Organic Pollutants (POPs) at sites worldwide. More recently the technology was selected as part of a pilot project with the United Nations Industrial Development Organisation (UNIDO), for treatment of POPs wastes in the Republic of Slovakia.

OVERVIEW OF THE GPCR TECHNOLOGY

Technology Description

Eco Logic's Gas-Phase Chemical Reduction (GPCR%) technology involves the reduction of organic compounds by hydrogen and some steam (which acts as a heat transfer agent and another source of hydrogen) at temperatures of 850°C or greater. Organic compounds are ultimately reduced to methane, hydrogen chloride or hydrogen fluoride (if the waste is chlorinated or fluorinated, respectively), and minor amounts of low molecular weight hydrocarbons (benzene and ethylene). The hydrochloric and/or hydrobromic acid is neutralized by addition of caustic soda during initial cooling of the process gas, or can be taken off in acid form for reuse, if desired. Cooled, scrubbed gas from the reactor ("Product Gas") is compressed and analysed. Product gas can then be reused as a fuel for plant components, or consumed in a burner.

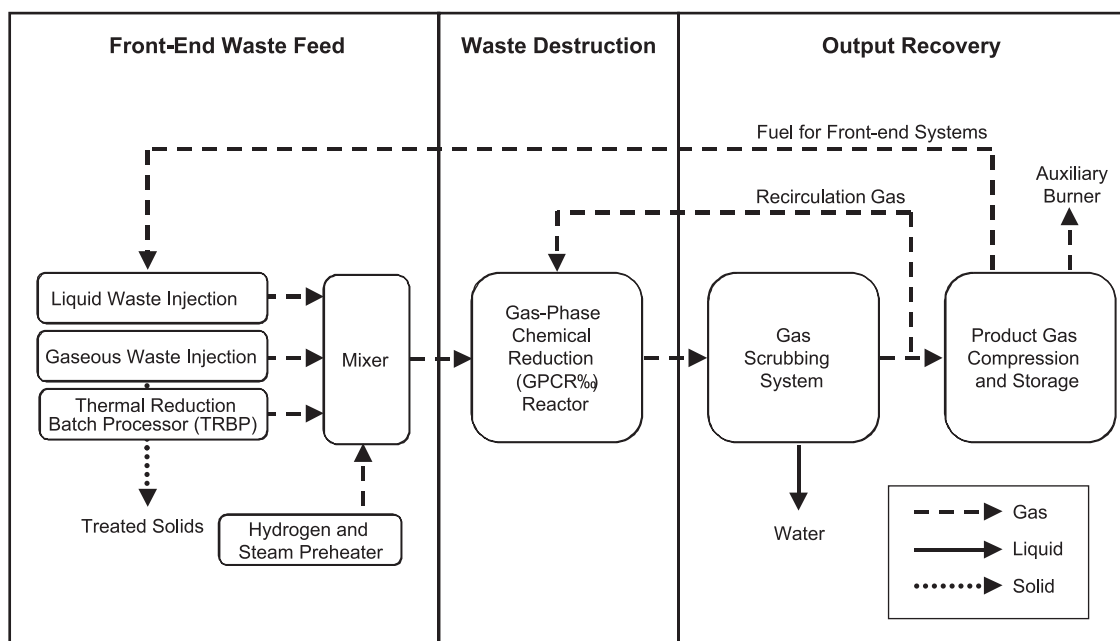


Figure 1: GPCR[®] Block Flow Diagram

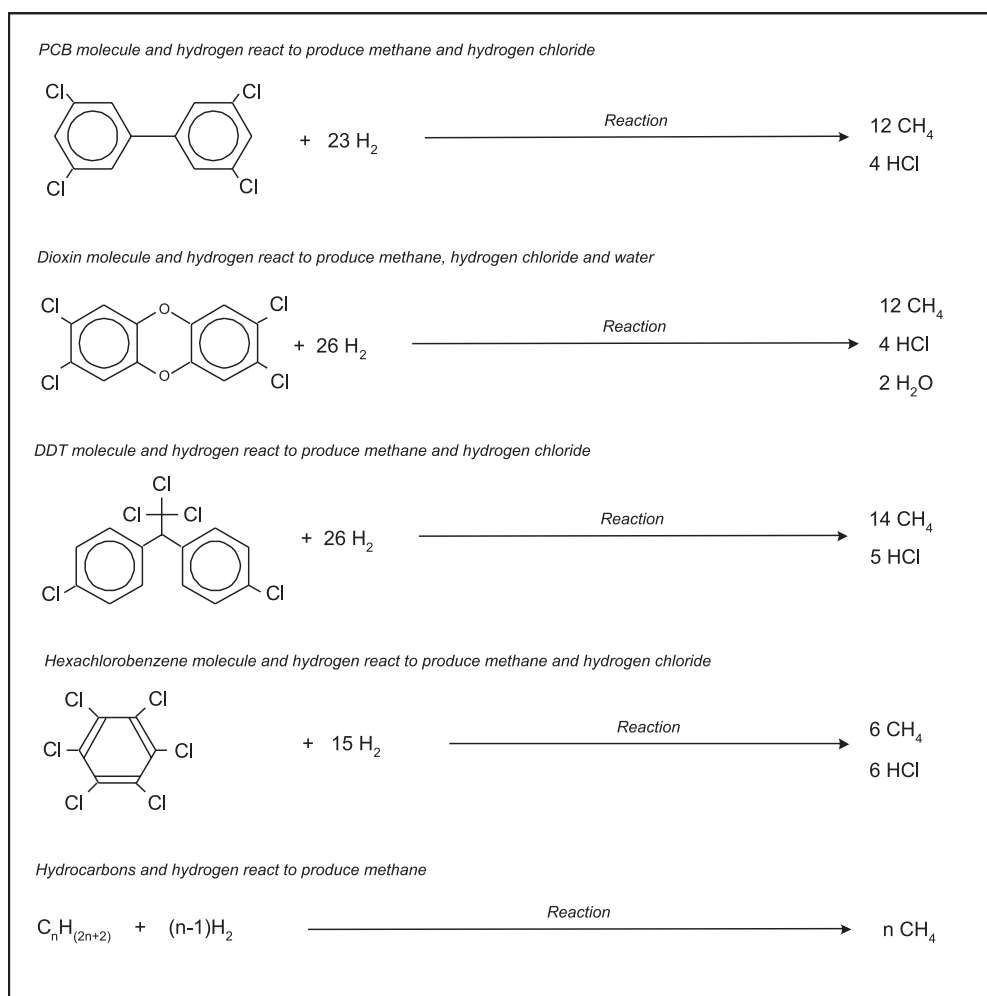


Figure 2: Gas-Phase Chemical Reduction Reactions

The GPCR% technology can be broken down into three basic unit operations: the front-end system (where the contaminants are rendered into a suitable form for destruction in the reactor), the reactor (which reduces the contaminants, now in gas phase, using hydrogen and steam), and the gas scrubbing and compression system (Figure 1). The front-end units will differ depending on the waste matrix. For example, bulk solids such as drummed chemicals, electrical equipment, spent carbon, etc., are placed into a Thermal Reduction Batch Processor (TRBP), which desorbs the contaminants from the solid material, and then conveys them to the reactor for destruction. Watery wastes and high-strength oily wastes are injected into a preheater that vaporises the liquids in an indirectly fired heat exchanger. The gases are mixed with hydrogen and steam to a temperature of 600°C prior to introduction to the GPCR% reactor.

In the case of soil and sediment treatment, contaminants are first desorbed from the solids using a thermal desorption device (of which there are many proven and available worldwide). The gas containing the contaminants is then condensed, the water removed, and the remaining concentrated contaminant liquid fed to the preheater and GPCR% reactor as a liquid waste feed.

Basic Chemistry of the GPCR% Technology

The GPCR% technology has been developed and engineered to deal specifically with halogenated waste streams, although non-halogenated streams can also be treated. Through the chemical reduction reactions, acid gases are created which can be neutralized or recovered. Figure 2 shows some examples of the reduction reactions for the destruction of a variety of chlorinated wastes using GPCR%. Unlike oxidation reactions, the efficiency of these reduction reactions is enhanced by the presence of steam, which acts as a heat transfer agent as well as a source of hydrogen. The water shift reactions produce hydrogen, carbon monoxide and carbon dioxide from methane and water. These reactions can be used at higher efficiencies to generate hydrogen for reuse in the system by subjecting scrubbed methane-rich product gas to high temperatures in the presence of a catalyst.

Most GPCR% experience has been with the treatment of chlorinated wastes (PCBs, pesticides) and to a lesser degree fluorinated wastes (chemical warfare agents and chlorofluorocarbon refrigerants). We have also treated a small quantity of iodine waste. In general the technology is well suited and well proven for halogenated waste streams. Of particular benefit is the fact that the waste streams do not require



dilution prior to destruction using GPCR%. For example, Eco Logic treated almost 100 percent pure hexachlorobenzene crystals using the commercial-scale GPCR% plant in Kwinana (Figure 3); no dilution or specialized pre-treatment was required. Similarly, the refrigerant R-12 (dichlorodifluoromethane) was treated in pure form using the GPCR% demonstration plant (diagram of reactions in Figure 4). This robustness is an advantage over other technologies that may require dilution of the material to accommodate the high halogen content.

Products From Waste Treatment

Contaminants entering the GPCR% reactor are reduced using hydrogen, heat and steam, resulting in a gas that is comprised of primarily methane, acid gases and hydrogen. This gas leaving the GPCR% reactor is scrubbed in two caustic scrubber towers to cool the gas and to remove acid, water, heat and fine particulate. The acid in the gas (HCl, in the case of chlorinated wastes) can be neutralized with a caustic solution (to create a salty scrubber water), or recovered for subsequent refinement/concentration to recyclable specifications for industrial reuse. During conventional hazardous waste treatment operations (PCBs, pesticides, etc.), Eco Logic has been permitted to dispose of scrubber water in a variety of ways, including discharge to a local irrigation system, discharge to a surface water body, and discharge to a municipal sewer.

The cooled and scrubbed product gas is a mixture of hydrogen, methane, carbon monoxide and other light hydrocarbons. Some of the product gas is reheated and recirculated back to the reactor, or through the TRBP as sweep gas. Excess product gas is removed from the system, compressed and temporarily stored. This stored product gas is chemically tested with on-line instruments and then used as fuel to heat system components such as the boiler, and as an input stream to a catalytic steam reformer as heating fuel for hydrogen generation (in situations where piped hydrogen gas is not readily available at the site).

System outputs generated during waste treatment activities are treated solids, water and product gas, all of which are clean, reusable or disposal products (Table 1). All outputs are stored and analysed prior to off-site disposal or reuse.

GPCR DEPLOYMENT IN THE SLOVAK REPUBLIC

The GPCR technology was selected for the treatment of PCB-contaminated material at an industrial site in the Slovak Republic, under a pilot project with the United Nations Industrial Development Organisation (UNIDO). Funding for a portion of the project was approved by the Global Environment Facility (GEF) in May of 2003.

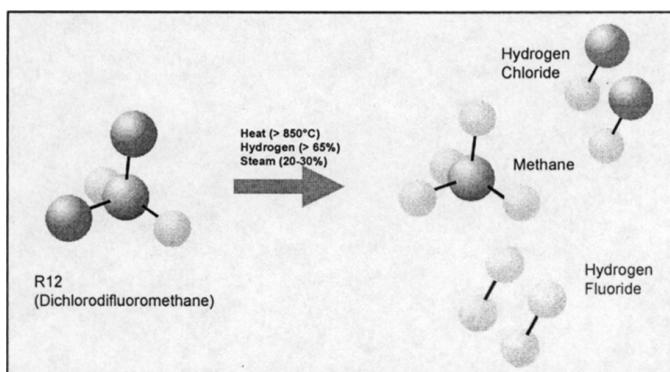


Figure 4: Gas-Phase Chemical Reduction of R-12 (Dichlorodifluoromethane)

Output	Source	Character	Post-Processing/Testing	Disposition
Treated Bulk Solids	TRBP	Metal components; residual inorganic carbon	Testing for waste-specific contaminants; leach testing	Recycling; unregulated landfill
Water	Gas Scrubbing System	Trace levels of low molecular weight hydrocarbons	Granular Activated Carbon (GAC) treatment; regulatory testing	Sewering; discharge to surface water body; irrigation
Product Gas	Product Gas Tank (collects scrubbed process reaction gas)	Hydrogen (60%); Methane (30%); CO (10%); trace amounts of light organic compounds	On-line testing using gas chromatograph	Fuel source for system components

Table 1: Summary of GPCR System Outputs

A semi-mobile GPCR plant (see Figure 6) will be used to treat PCB wastes currently located at an industrial facility in the Slovak Republic, as well as other wastes that may be brought in from locations throughout the country. Specific waste types include solid residues from PCB manufacturing, PCB capacitors, PCB-contaminated transformer oil, and PCB-contaminated sediment from an adjacent discharge channel. The following sections describe the feed systems that will be used in order to treat these varying types of material using the GPCR equipment.

Feed Systems – Solid Residue Wastes and Capacitors

Contaminants must be in a gaseous form in order to be reduced in the GPCR% reactor. While liquid wastes can be preheated and injected directly into the reactor on a continuous basis, contaminants on solids must first be volatilised from the solid. Bulk solids and drummed chemicals are placed in a TRBP, which desorbs the contaminants and then conveys them directly to the reactor for destruction.

The TRBP consists of an externally heated oven-type chamber. Organic contaminants contained in the liquids,

solids and sludges are volatilised and the organic vapours are swept into the reactor by the hydrogen-rich hot recirculation gas.

In the case of capacitors, the material remaining in the TRBP following treatment will be the metal casing and other inorganic components of the capacitors. In the case of treatment of the PCB solid waste residues, experience shows that almost complete volatilisation of the material will be desorbed from the drums; any material remaining in the drums will be inert inorganic carbon.

Feed Systems – Soil and Sediment

As noted above, treatment of soil and sediment is typically handled using a separate front-end desorption device. (While soil and sediment can also be treated using the TRBP, the TRBP operates in a batch mode, and as a result provides a lower throughput than is typically required for soil and sediment projects.) For large soil and sediment projects, a thermal desorption device is used to desorb the contaminants from the soil and sediment. The off-gases is then condensed, the water fraction removed, and the concentrated contaminant liquid treated in the GPCR% reactor. A diagram of this approach is provided in Figure 5.

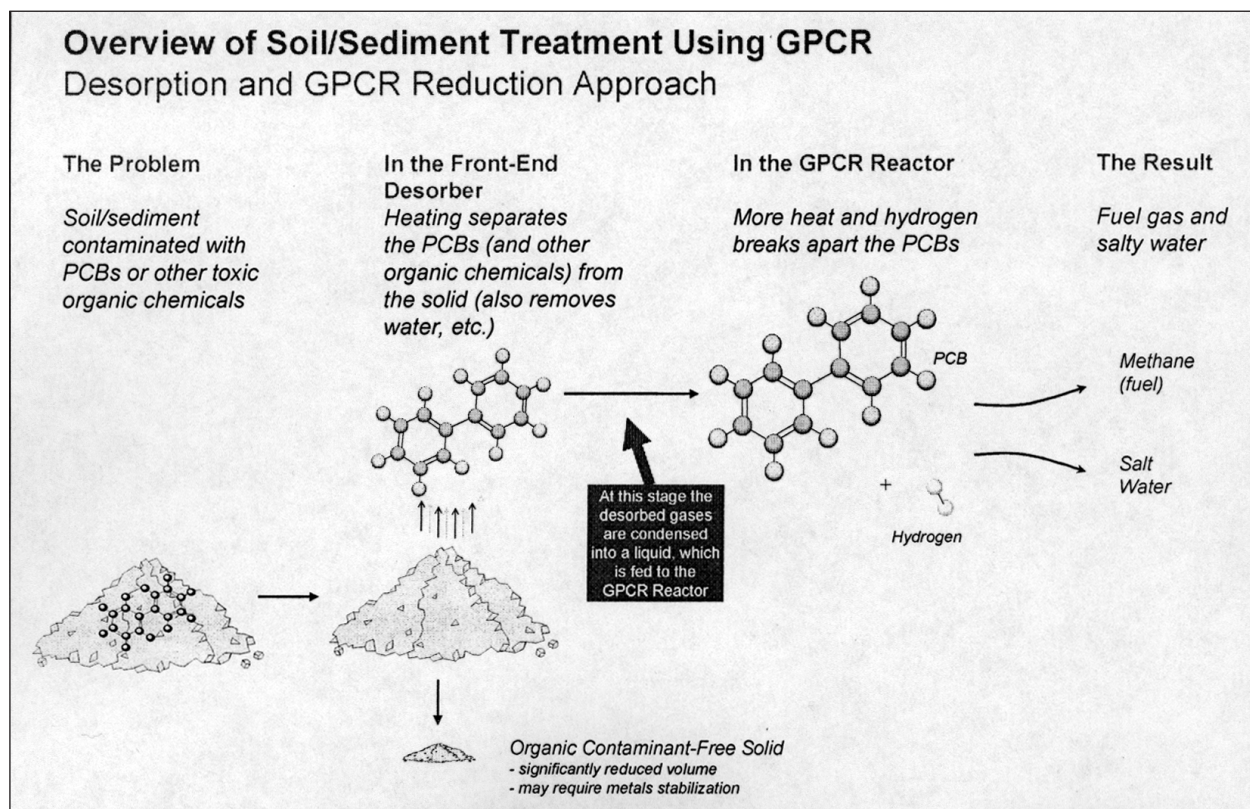


Figure 5: Overview of Soil/Sediment Treatment Approach Using GPCR

Project	Contaminant	Destruction Efficiency (%) *	Target Criteria (%)
Bay City (oily water – 3 tests)	Tetrachloroethene	> 99.99	99.99
Bay City (oil – 3 tests)	Tetrachloroethene	> 99.99	99.99
General Motors of Canada Limited (PCB Oil – 3 tests)	PCBs	99.9999996	99.9999
	PCBs	99.9999985	
	PCBs	99.9999808	
	Chlorobenzenes	99.9999836	None
	Chlorobenzenes	99.9999972	
	Chlorobenzenes	99.9999971	
PCB Oil (Kwinana Regulatory Testing)	PCBs	99.999998	99.9999
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	99.999999	99.9999
Refrigerant Treatment (CFC R-12 – 1 Test)	Dichlorodifluoro-methane	> 99.999	99.99

Table 2: Efficiency of Hazardous Waste Treatment using GPCR δ

* Note that these destruction efficiencies take into account contaminants in the solid and liquid outputs, in addition to the stack gas. The exception may be the Japanese Regulatory Testing, where we are unsure of whether solid and liquid outputs were included in the calculation.

TECHNOLOGY VALIDATION

Table 2 provides data from destruction of halogenated wastes using GPCR%. Note that much of the data come from regulatory testing conducted during treatment of high-strength PCB oil at a General Motors of Canada facility in Ontario, Canada. This data was audited by the Provincial Government (Ministry of the Environment). Data from other projects has also been verified by third-party review, such as regulatory authorities in Australia and the US National Research Council.

The technology has been developed and operated at commercial-scale for conventional hazardous waste treatment applications. Eco Logic has operated two full-scale commercial plants in the past. A third commercial plant (semi-mobile scale) has been recently constructed by Eco Logic's partners in Japan (Figure 6). Two demonstration-scale plants are housed in Japan and at Eco Logic's head office in Rockwood, Ontario, Canada.

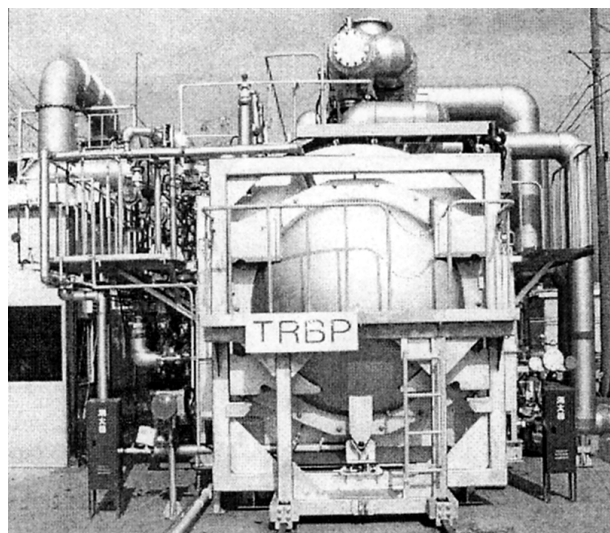


Figure 6: Semi-Mobile GPCR δ Plant in Japan

THE BCD PROCESS AND THE SPOLANA DIOXIN PROJECT

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INTRODUCTION

The BCD process has been presented at the HCH and Pesticides conferences in the past, the most recent being the presentation of IHOBE on their project for treating HCH deposits in the Basque country.

The focus of this presentation will be the real life application to a very complex and multifaceted project in the Czech Republic where the BCD process will be used as part of the overall remediation of an area in the Spolana Chemical works, in which buildings and surrounding soil are heavily contaminated with chlorinated hydrocarbons and significantly high levels of dioxins.

THE BCD PROCESS AND ITS DEVELOPMENT

The process was developed by the US EPA in a programme in the 1980ies, aimed specifically at developing alternatives to incineration for the destruction of chlorinated hydrocarbons, principle targets being PCBs and pesticides, and the remediation of sites contaminated with these pollutants.

A very simplified equation (Figure 1) shows the overall reaction. It is described as a hydrogen transfer reaction, in which hydrogen splits from the carrier oil, a petroleum oil under the influence of molten sodium or potassium hydroxide, and the catalyst, which was initially fine carbon. Hydrogen chloride formed by the hydrogenation of the chlorinated organic molecule reacts further to produce sodium chloride. The overall reaction is exothermic.

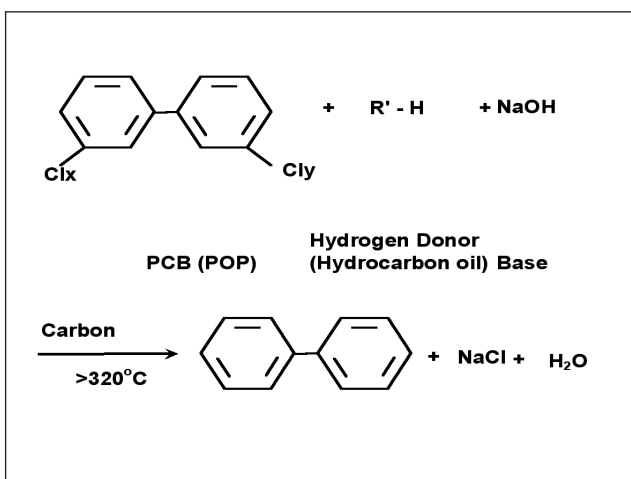


Figure 1: The BCD Reaction

When treating PCBs biphenyl is produced. The de-chlorination of polychlorinated compounds is in the main sequential. However the yield of the parent molecule is quantitative since cracking also takes place. One area on which the developers, and principally GCMS experts at Wright State University, concentrated were to investigate whether or not secondary chlorinated species were left at the end of the reaction. It was exhaustively verified that this is not the case.

The US EPA handed over the basic chemistry and license rights to private industry to develop and use in industrial scale operations, either directly to US companies for application on superfund site remediation or to international companies through the BCD International Group.

Our team obtained licenses in 1994 and began process development. We established a development laboratory in Melbourne, Australia and constructed a high-pressure pilot reactor with a 200 litre working volume. Both in order to speed up the reaction, especially the “tail-end” and better to separate and treat the reaction products, our development employed other catalysts, such as long chain alcohols, and refined mineral oil fractions instead of heavy fuel oil which have better physical properties. The pilot reactor was used both in trials in New Zealand and in a small project in Australia.

The remediation of contaminated sites not only involves chemicals and chemical residues but inevitably large quantities of contaminated soil and building materials. From the beginning the BCD process concentrated on this problem and evolved a two-step process. The concept is to use a first step to desorb and strip the organic contaminants from the bulk materials and concentrate them in a small vapour stream. The vapour stream is condensed and filtered, producing a much smaller stream of concentrate, which is treated chemically in a second step where the POPs are actually destroyed.

The two steps run parallel to each other, but are not directly interlinked. This provides more processing flexibility and better quality control. This simplified process flow (Figure 2), is typical. The bulk materials, where necessary, are first broken down to particles of less than 30-50 mm. This speeds up the heat penetration and desorption. Low cost alkali such as lime can be added to the matrix. This addition can be favourable to de-chlorination. By heating to temperatures above 500°C all the organic materials break down.

The heating takes place in a continuous indirectly heated rotary kiln. For all practical capacities the heating utilises hot flue gases from combustion of natural gas or light fuel oil. Heat flux rates from electrical heating are too low to have efficient, economic throughput rates. Air and combustion gases are prevented from contacting the contaminated materials by mechanical seals and inert purge gas, otherwise in the presence of oxygen, dioxins could actually form inside the rotary kiln. The design and maintenance of the mechanical seals, which seal the internal rotating kiln from the outside environment, are critical to the operation.

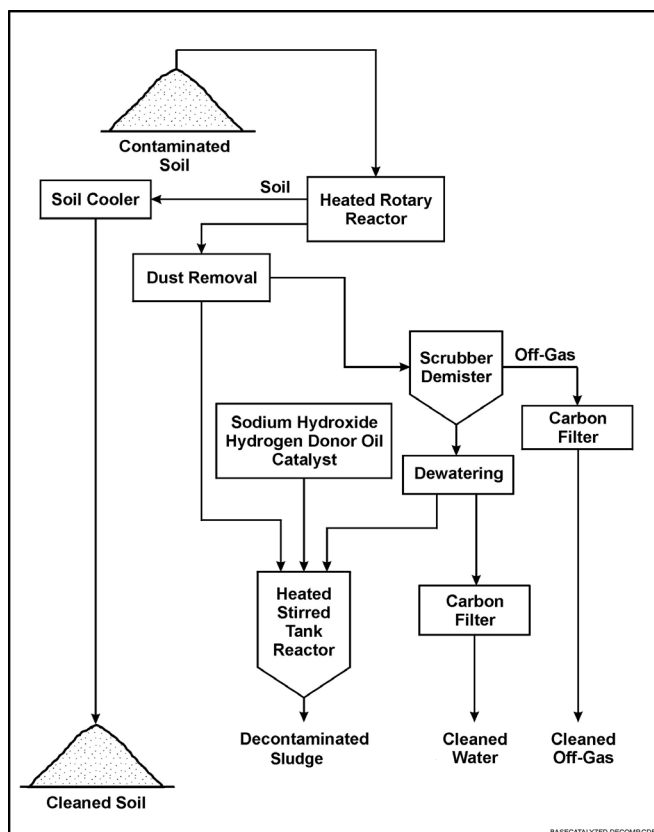


Figure 2: Simplified BCD Process Flow

If soil is the matrix there will be an appreciable water vapour stream leaving the kiln. The vapours are filtered and condensed and separated. The residual inert gas, which is nitrogen, then passes through a series of activated carbon filters before being emitted to the atmosphere. It must be emphasised that inherent in this type of non-incineration process is a significant advantage. The actual flow of treated off-gas leaving the process stack is orders of magnitude smaller. Typically the BCD process would emit 100 m³/h of off-gas, compared with tens of thousands of m³/h typical from an incinerator. The concentration limits on pollutants such as dioxins is the same, so that in terms of mass flow, incinerators emit significantly larger quantities.

Water is separated from the condensate and treated separately. The organic condensate, sludge and fine dust are discharged to sealed containers and stored pending treatment in the BCD reactor.

The BCD reactor is in contrast to the desorber a batch process, in which the reagents are added and allowed to react as long as is needed until the destruction of the POPs is complete. We are often looking at concentration changes of 4-5 orders of magnitude. To try and achieve this in a continuous reactor for this type of reaction would be impossible. The batch reaction can also be sampled and analysed on-site to test the degree of completion, and dumping of the reagents takes place only when the destruction efficiency has been confirmed. Reaction times are several hours, with a total batch cycle time of about eight hours. On site analysis and QC depend on the contaminant types and the analytical tools available. In all cases no residues leave site until we have external analytical confirmation.

There is no limit to the concentration of PCBs etc. which can be treated. The only limitation is the solids content in the stirred reactor. We stir reaction mixtures with 30% solids. If the degree of chlorination is high, then proportionally less is added to each batch.

The current design with thermo-oil heating and cooling reduces the potential for fire, since only in the reactor during the reaction is the oil above its flash point. The reactor is cooled before emptying.

Figure 4 shows the combined operational units at the Olympic site in Australia. This was an irregular landfill site where drums of waste HCB had corroded, leaving behind contaminated soil and concentrated chemical residues. Dioxins were a prime problem at this location.

Figure 5 lists the projects, which used BCD technology.

In 1992 the operations began of a BCD licensor in Queensland, Australia, treating PCB contaminated transformer and hydraulic oils. This operation continues to operate, during which time it has played a significant role in reducing Australia's stockpile of PCBs.

Figure 6 shows the operation at a US navy site on Guam, treating PCB contamination. Mainly pure PCBs are treated in Mexico.



Figure 4: Olympic Site, Australia



Date	Organisation	Description
1989	US EPA	Development of Chemistry by the US EPA
1991		1st patents granted
1991	Soil Tech, USA	Wide Beach Superfund Site (NY) 42 000 t soil, PCBs (5 000 ppm)
1992		Outboard Marine Superfund (IL) 13 000 t soil,

Date	Organisation	Description
1992-ongoing	BCD Technology	BCD Technology opens commercial facility, Queensland, Australia
1993	US EPA	Koppers Superfund Site (NC) Clayey soil, PCB and dioxins
1995		Smith Farm (KY) 30 000 t soil, PCP, pesticides
1996	ETG (USA)	Binghamton Superfund Site (NY) 3 000 t soil, PCP, dioxins
1997		Dow Chemical, wood preservatives (MI) 500 t soil, PCP, DDT, dioxins

Date	Organisation	Description
1997	US Navy/IT Corp	US Naval Base, Guam 10 000 t soil, PCBs
1998	ADI Limited	Wood Preservatives Site (NZ) Soil, pesticides, dioxins, pure chemicals
2000-2002	IHOBE	Lindane reduction (Bilbao, Spain) 3 500 t lindane converted to TCB
2000	Enterra (Australia)	Moe Power Station Site VIC, AUS PCB contaminated soil
2001-2002	Enterra (Australia)	Olympic Site, NSW, AUS
Current	Shaw Group (USA)	Warren County Landfill (NC) 40 000 t soil, PCBs and dioxins
Current	S.D. Meyers (MEX)	BCD treatment facility (Mexico) PCB contaminated oil

Figure 5: Chronology of BCD Applications and Activities



Figure 6: BCD operation at a US navy site on Guam

SUMMARY

It is a non-incineration technology, with tiny emission streams, each one passing through activated carbon

It is simple in its concept, its operation and as a batch process maintains good quality control.

Since its first application in 1991, more than 100,000 tons of contaminated materials and residues have been treated.

DIOXIN CONTAMINATION, SPOLANA CHEMICAL WORKS, CZECH REPUBLIC

The Spolana chemical works is a large chemicals complex on the bank of the river Elbe, north of Prague. Manufacturing at this site goes back a hundred years and like many chemical developments in this region of Germany was based on chlorine chemistry derived from the electrolysis of brine. PVC is still one of the main products at this site.

Insecticides, herbicides and fungicides were produced in areas of the factory. In the two remaining buildings, which are the focus of our remediation project, the active components of some of these products were produced in the 1960ies, materials such as pentachlorophenol and the sodium salt of 2,4,5-trichlorophenoxyacetic acid.

Another activity was a process developed to recover trichlorobenzene from large quantities of residual HCH residues left over after the extraction of the gamma-isomer in the production of Lindane. It went unnoticed at the time that the de-chlorination of the HCH residues produced trace amounts of dioxins including 2,3,7,8-TCDD. Recycling of mother liquors resulted in a build-up of concentrations. Steam distillation was used to separate the TCB, which was vented inside the building, resulting in spreading of high concentrations of contaminants throughout the whole working area.

Increases of serious illness among the workers and comparison with similar developments in other countries led to the total shut down in 1968, virtually from one day to the next, leaving the buildings untouched, without any decommissioning having taken place.

In the years following the land outside the larger of the two buildings was used to store barrels and other vessels containing poisonous and corrosive chemicals, leading eventually to leakage and serious soil contamination. The building interiors are essentially as they were left, except for a covering of thick dust, where dioxin concentrations of 20,000 ng/g, that is 20 million ng/kg have been analysed.

A number of risk analyses and feasibility studies have been performed over the last years, and provided the basis for a remediation design.

Figure 7 from inside the buildings shows the buildings and their contents together with some of the investigative work performed. Work was performed to assess degrees of penetration, and whether surface scabbing could remove contamination. Contamination was shown to have penetrated at high concentrations through the concrete.

Solvent washing of metal surfaces as well as abrasion failed to eliminate residual dioxins. The plaster on the inside of the walls has high dioxin contents. The brickwork

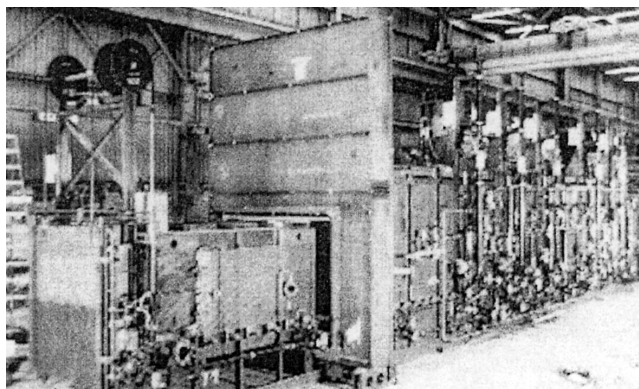


Figure 7: Inside the buildings

behind the plaster has much lower levels, but still too high to allow land-filling of this brickwork.

Before any decontamination work can begin the building and surrounding area will be sealed off with a steel building enclosure.

We view the most serious potential hazard to the local population would be dust emissions. Not only will the work areas be totally enclosed, but at all times an under pressure relative to the outside will be maintained in the enclosure to ensure leakage of air into the enclosure and to prevent any leakage outside. The size of this exhaust system will be in excess of 200,000 m³/h. Exhaust air will pass through both dust and activated carbon filters.

Because of the high concentrations and health risks associated with the insides of the buildings and the extensive plant removal required we distinguish between decontamination and demolition phases. In the first phase the contents of the buildings the plaster and dust will be removed using industrial vacuum cleaners, and hand and hydraulic tools. During this work the sealed building shell will act as an additional barrier to prevent dust emissions.

Only when the high concentration surfaces have been removed will the building demolition work begin. There is a space problem on-site and no possibility or desire to store large quantities of contaminated materials, so that the rate of decontamination, and especially the rate of demolition

and excavation will be determined by the feeding rates to the treatment plants.

The clean-up criteria have been set at 0.2 ng/g for soil and 5 ng/g for building rubble. In practice materials will be treated consecutively so that 0.2 ng/g will apply throughout.

Indirect thermal desorption and BCD treatment of concentrates and chemicals as previously described will be used to treat the main bulk materials and chemicals. Pure chemicals and residues will be fed directly to the BCD reactor. Metal parts, cut up into manageable pieces, cannot be physically handled in the ITD, and so will be treated in a stationary high temperature furnace, again heated with exclusion of air. This type of plant is being used to decontaminate metal parts such as artillery shells, which had been filled with chemical warfare agents.

Any water arising out of the treatment operations, mechanical work or decontamination of protective clothing will be treated in a batch wastewater treatment plant; flocculation, oxidation with H₂O₂, followed by carbon filtration.

The Spolana dioxin project is a very complex one. Very many different tasks will need to be performed before the job is completed on a wide variety of different materials. The concentrations existing at this site of such high toxicity pollutants have seldom been seen at any site remediation to date.

This aspect and the need to protect the local population dictate the sealing off of the area and will dictate the operating and health and safety procedures for our workers. At this point in time we are establishing such procedures and evaluating environmental impact with public and regulatory authorities in the Czech Republic.

We can expect to be confronted with a host of technical and operational challenges in the coming period and although the team put together will be able to fall back on a wealth of operating experience, new problems can be expected requiring new solutions. In practice no remediation job ever goes completely as planned!

Nevertheless, we would hope in two years time to be able to report that a sizeable part of the work has been done and that we are well on the way to a successful completion.

DETAILED REVIEW OF POPS ELIMINATION TECHNOLOGIES FOR THE CEE REGION

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Establishing elimination capacity for persistent organic pollutants (POPs) and obsolete pesticides for countries in the CEE Region is a complex process, involving a number of strategic steps into which national capacities and strategies, affordability and actual amount of stored material must be factored in. No matter which technology is adopt-

ed for implementation, mandatory planning actions and public awareness actions must be completed and carefully assessed prior to any initiatives.

In the early 1990s, the CEE Region was regarded more or less as one region. During the mid 1990s a number of countries entered the EU enlargement process ultimately leading to full EU membership from May 2004. In between, e.g. Bulgaria and Romania have been declared as new candidate countries with expected adoption in the EU community by year 2007. The ongoing transformation of the region and eastward movement of EU borders make a new division of Europe inevitable. The new EU members will have to adopt the EU environmental acquis and follow in line with community decisions, such as the Stockholm

Technology	Time	Actual site visit area
Container-based Incineration System (CIS)	1 March 2002	Chemcontrol A/S Kommunekemi, Nyborg, Denmark
Base Catalysed Dechlorination (BCD)	9–10 April 2002	Enterra Pty Ltd. Sydney, Australia
Gas Phased Chemical Reduction (GPCR)	26–27 June 2002	ELI Eco-logic Inc Toronto, Canada
Cement Kiln Incineration (CKI)	27–28 August 2002	NORCEM and Noah Oslo, Norway

Table 1: Time schedule for performed detailed review of POPs/OPs elimination technologies.

Convention (SC). The new EU member states will furthermore have increased access to cohesion funds based on national priorities. To a still larger extent, non-EU member states like e.g. Ukraine, Belarus and Albania will also try to affiliate national legislation and regulatory framework into the EU acquis, although external available funding into e.g. the Stockholm Convention anticipates still to rely on national funds in combination with bilateral and/or international funds.

The report performs a detailed technical, environmental and economic review of in total four pre-selected incineration and non-incineration destruction technologies for POPs. The pre-selected technologies are all commercially available on the world market and have all been reviewed in operational mode. The pre-selection process involved a global screening of available POPs elimination options and, based on in-meeting with major NGO organisations like Greenpeace International, Pesticides Action Network-UK, International Pesticides Elimination Network (IPEN) and the International HCH & Pesticides Association, four potential technologies were selected for independent, but comparable review. These were **Container-based Incineration System (CIS)** and **Cement Kiln Incineration (CKI)** representing the incineration-based technologies and **Gas Phased Chemical Reduction (GPCR)** and **Base Catalysed Dechlorination (BCD)** representing the non-incineration technologies.

The selected technologies have a number of uniform features of importance for the overall approach by the report (although the cement kiln option is not defined as a dedicated structure, but of key interest due to extensive distribution and actual operational knowledge related to this technology in the CEE Region). These are that the selected technologies are dedicated to POPs, obsolete pesticides or even hazardous waste elimination, experiences from on-site elimination of POPs substances, detailed mapping of possible point sources for uncontrolled emission (air, waste residues and effluent water), in nature making these attractive for small scale investment and organisational settings, and for at least two of the technologies (CIS and GPCR), on-site implementations are ongoing in the CEE Region in Latvia (CIS) and Slovakia (GPCR).

The detailed review involved a number of environmental, technical and economic review criteria, which have been reviewed in advance and agreed upon by major advisory NGO organisations. The environmental criteria covered materials used for construction of the elimination plant, means of operation, efficiency of the elimination process, emissions to air, water and soil and residues. The technical review criteria included environmental and economic impact, capacity of the technique, comprehensiveness, robustness and maintenance possibilities and expenses, capacity building, supply lines, generation, residual products, occupational health and operational risks, while the economic criteria included organisation, transfer of know-how, capacity, logistics, process residues, demands, direct and in-direct costs assessment.

The four pre-selected POPs elimination technologies were carefully reviewed on-site by a team of not less than two experts, covering the environmental, technical and economic aspects. The reviews were performed according to Table 1.

Based on an evaluation mask taking all reviewed criteria into balanced consideration, the following can be concluded:

- The CIS and GPCR POPs elimination technologies are found equal in appropriateness, market availability, affordability and operational performances, taking into account possible environmental impact, use of supply lines and risk potential;
- The BCD technology is characterised by having lower capacity, high use of supply lines and relatively less affordable; while
- The cement kiln incineration is characterised as "a way through", but has several disadvantages like no matured overall business sector (less degree of sustainability) where mergers are day-to-day life seriously affecting possible investment into this kind of technology. Furthermore, CKI is not a dedicated technology, too many resources are used for other purposes than purely POPs elimination, etc. Finally, high investment costs into pre-treatment are needed, significantly reducing the economic attractiveness of this technology, although recent test results from stack-emission in for instance Poland show none or little (below

EU admissible levels) impacting substances generated from the co-disposal activity.

Finally, the report concludes that proper selection of elimination technology is one part of the overall process enabling countries to deal with their own POPs/OPs waste problems in compliance with national strategies and policies and international environmental binding instruments (like the Stockholm and Basel Conventions). In many cases, the final choice of technology depends on "secondary" issues like endorsement of donor policies, amount and character of available funds, political tendencies and pressure from private industries and investors encouraging the responsible authorities to implement commercially viable solutions in a

broader perspective, based on more than just a minor waste fraction such as POPs and obsolete pesticides.

Nevertheless, as an overall facility, international environmentally binding instruments (protocols, conventions etc.), and their related mandatory actions for Parties, have traditionally been the global modality to move forward significant actions within major environmental problems like the Montreal Protocol on ODS, biodiversity etc. Taking into account the fact that the expected time span from final decision on establishment of elimination capacity to day-to-day operation is normally 6-8 years, the political process and constant public awareness are of utmost importance in supporting the process all along.

CURRENT SITUATION ON UTILIZATION OF DISCARDED PESTICIDES IN THE REPUBLIC OF LATVIA

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At the previous International HCH and Pesticides Forum in Poznan, March 13 -15, 2001 I presented major issues of the discarded pesticide problem in the Republic of Latvia. Today my presentation could be very short – no change at all.

In Poznan I explained that in 1997 – 1999 in Latvia all obsolete pesticides were collected from all over the country and transferred into two specially constructed interim storages for hazardous waste (HW). The plan was to keep pesticide waste there approximately till year 2002 when we expected to push into action a hazardous waste incineration facility and to start destruction and final disposal of pesticide waste.

Unfortunately we were too optimistic in our plans – in reality there were a lot of delays. The main delay was caused by the lack of public acceptance of the selected sites for installation of the incineration facility. In general, the public agrees that HW management infrastructure objects are necessary for the country, but not in our village, town, e.g. – **not in my back yard.**

In the long run somehow we succeeded in site selection in the small town of Olaine, which is situated approximately 25 km south of Riga, the capital of Latvia, and which is the main centre of Latvian chemical and pharmaceutical industry. At present, after some delay, construction works and installation of the incineration facility are finished and we are now in the process of obtaining necessary permits and of testing installation procedures. We expect to start destruction of the discarded pesticides by the end of this year.

When we are speaking about the public opinion about the location of the HW management infrastructure objects it is necessary to look at the opinion of

- local municipalities, local officials and politicians,
- inhabitants.

The development of the concrete HW installation depends on both parties. First of all it is necessary to say some words about the role of local municipalities. This role is very significant, but at the same time in our country local governments have almost no legal responsibility for the process of the development of HW management system in the State.

According to Latvian legislation, the State is responsible for HW management and in this case the Ministry of the Environment is authorized to co-ordinate and organize all practical issues, including the organization of construction and management of HW recovery facilities and landfills. At the same time, according to the Waste Management Law the local municipalities only shall take decisions regarding the location of the new HW recovery facilities and landfills. This means that responsibility of the local municipalities for the process of formation of a HW management system in the country is very minimal and if concrete activities of this process do not offer them sufficient benefits, municipalities are not interested in having the HW management infrastructure objects (incinerators, landfills, storages, etc.) in their territories. At the same time any location of HW infrastructure object is impossible without acceptance and positive decision of a local government.

Therefore site selection processes always start with negotiations with municipalities about conditions under which they can accept HW management infrastructure facilities. If the Ministry manages to receive acceptance from the municipality, it could start the EIA process, which is obligatory for an erection of HW management infrastructure facilities. It is worse when, at the beginning, the municipality's decision was positive for erection of such a facility and the Ministry has spent a lot of time and financial means for the EIA process, in result of which the selected place was recognised as suitable, but later on under

publics pressure the Municipality rejects his previous decision and said "No". In this case it is necessary to start the whole process anew. Of course, usually not only one but several places are involved in the EIA process, but if at the end of the EIA process some places could not be accepted due to the objective reasons but other ones are rejected by the local municipalities, there is only one way – to start the whole process anew. Such a situation took place in the case of site selection for a hazardous wastelandfill in Latvia.

If we speak about the local population, then almost always it is **"not in my backyard"**. Sometimes a public "NO" obtains a very active and even aggressive response (meetings, pickets, protest letters to the highest State institutions such as Parliament, Cabinet of Ministers, President, and even court cases). Very typically is the situation where the public interest in possible future activities is very weak at the beginning of the site selection process when, according to the requirements of the Law on Environment for Impact Assessments public hearings are organised in all potential sites. Usually the interest grows just before the final decision of the site selection or even after construction works have been started. In these cases the public attitude as a rule is negative and objective explanations by neutral specialists or state officials are ineffective, whereas activities of people who agitate against planned constructions of a HW management facility work very well. Very often politicians will exploit this situation. Especially, such politicians increase activities just before elections. Taking into account that in Latvia elections take place every two years, site selection processes for HW infrastructure objects are extremely complicated.

Main lessons learned from experiences of solution of the discarded pesticide and other HW problems in Latvia – in case when you have all necessary resources (financial, human, technical), your staff is adequately skilled technically, you have almost a perfect project management but if you have not planned the public awareness activities seriously, and you have no public acceptance of the project you cannot have a fully successful hazardous waste (discarded pesticide) project or even you could face complete failure. To be successful you cannot economise on public information campaigns and education, but even in the case when you have done all your best you cannot be quite sure about the results, as the principle "not in my backyard" works anyway.

Although the installation of the incineration facility is finished we cannot say that the local population has accepted this. People follow their protests and unfortunately our information and explanation activities are not successful enough. Very often people are unwilling to listen to us. We understand that the communication situation has to be improved and therefore we have applied for assistance in Denmark – at the Danish EPA (DANCEE), since Denmark has a rather long communication tradition in the area of HW management. At present we, together with Danish specialists from the company COWI, have started to prepare a Communication Strategy for dealing with HW in Latvia.

We do hope that step –by step we will manage to improve the situation and build up the citizens' confidence and trust in the communication and information provided.

SUMMARY OF SESSION ON PHYTOREMEDIATION FOR PESTICIDES CONTAMINATED SOIL

Steve Rock and Konstantin Terytze

- Vicente Santiago Fandino described role of the United Nations Environmental Programme (UNEP) and the International Environmental Technology Center (IETC). The speaker explained the range of uses of planted systems for cleaning and mitigating environmental problems. Green roofs were shown that sequester carbon from the atmosphere; constructed wetlands that trap sediments, filter contaminants, and degrade organic pollutants. Reforestation has helped contain mine wastes and provide treatment for biosolids, as well as providing effective runoff protection for streams from fertilizers and pesticides.

- According to Werner Kordel, in Germany the safe soil regulations were developed by looking at plant uptake. Studies were done with a variety of plants and metals, and the measured uptake by those plants was determined to be the bioavailable limit for those metals, with an added 5x safety factor. This methodology could be used as a protocol for other countries and other contaminants of concern, such as HCH and pesticides.

- Kabul Zhambakin explained that in Kazakhstan a phytotechnology project is underway to find a national solution to the widespread problem of pesticides applied to soil to combat locust and other pests. In the first year of this three year

project site characterization is underway at representative sites, including contaminant concentration across the site and at depth. Plant surveys are also done, of species and coverage, to determine if any of the native or local plants growing on the sites are effective in degrading or taking up the target contaminants. This work, in partnership with USEPA and the Kansas State University, aims to provide the beginning of a plant library of effective plants and a model protocol for how to conduct such research in New Independent States on the remediation of soil applied pesticides.

- Barbara Zeeb pointed out that the Royal Military College is charged with cleaning one remnant of the cold war - a series of military sites that cross Canada in a set of lines. One line is far north, another is across the middle of the country. During site characterization, plants were discovered that seem to extract DDT and PCBs from soil. Greenhouse experiments confirm the field observations, that these chlorinated compounds do move into plant tissue in measurable quantities. This is contrary to previously accepted belief that compounds with very high octanol water coefficients would not be taken into plants. The mechanism for this uptake is not understood currently, and is the subject of further research. When this process is more understood, it could possibly be used to identify plants that could be used for the uptake and extraction of HCH and pesticides.

- According to Herco van Liere, phytotechnologies and Bioremediation often requires long time periods of open access to a contaminated site to be effective. Activities like tilling, watering, and sampling in most cases require clear surface area. This talk described a successful enhanced bioremediation project accomplished underneath an active container handling site. A system of piping was installed to add needed biodegrading elements, and to sample for treatment efficacy. The HCH from previous industrial lindane production was degraded to benzene and monochlorobenzene, which are subsequently removed and treated in a water treatment system. This innovative installation shows that limits to biological solutions can be overcome in the treatment of pesticides.

PHYTOTECHNOLOGIES AND ENVIRONMENTAL MANAGEMENT

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UNEP'S INTEREST IN PHYTOTECHNOLOGY

The United Nations Environment Programme (UNEP) recognises the importance of streamlining the integration of environmental and development strategies to make them more coherent in achieving sustainable development objectives. A central role for UNEP is to encourage decision-makers in government, industry and business to develop and adopt policies, strategies and practices that are cleaner and safer, use natural resources more efficiently, and reduce pollution risks to human beings and the environment. Within UNEP, the Division of Technology, Industry and Economics (DTIE) is responsible for promoting the adoption and transfer of environmentally sound technologies and management practices.

In support of this, and as part of UNEP/DTIE, the International Environmental Technology Centre (IETC) focuses on issues related to urban environmental problems and the management of freshwater basins. IETC pursues a results-oriented mandate, which involves:

- Improving access to information on environmentally sound technologies (ESTs)
- Fostering technology cooperation, partnerships, adoption and use of ESTs, and
- Capacity building.

IETC's principal interest in promoting the concept of phytotechnology relates to water, urban environmental management issues and climate change. Linked to this is the integrated approach of the Centre in supporting the principles and concepts of biodiversity and sustainable development.

PHYTOTECHNOLOGIES:

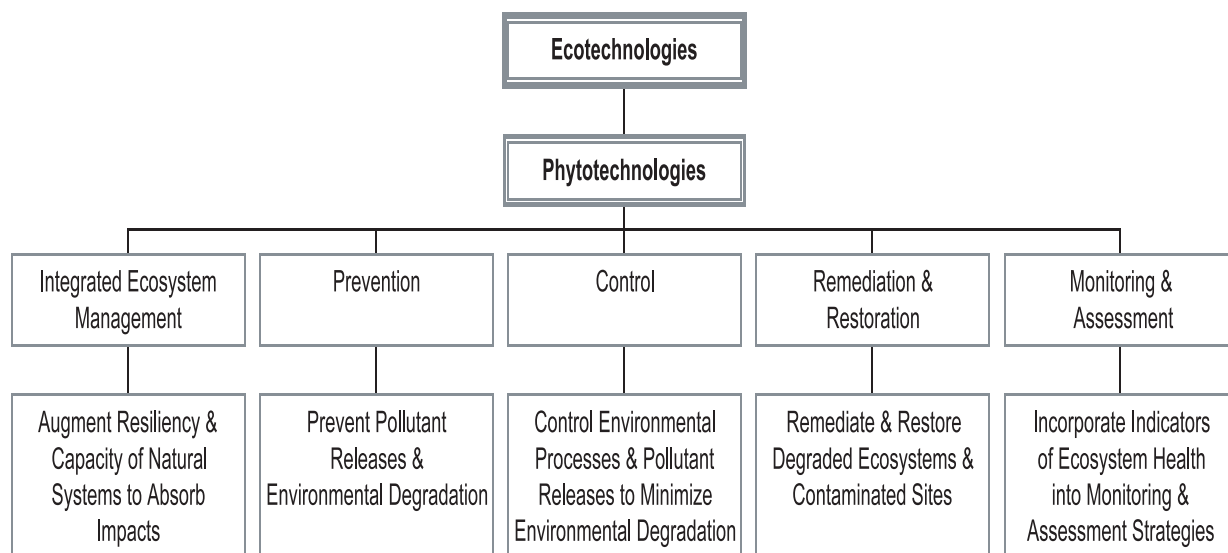
The term **phytotechnology** describes the application of science and engineering to study problems and provide solutions involving **vegetation**. Although the term is not widely used, it is useful in promoting a broader understanding of the importance of plants and their beneficial role within both societal and natural systems. An important underlying concept is the use of plants as **living technologies** to help address environmental challenges.

Phytotechnology applications employ ecological engineering principles and hence are considered to be ecotechnologies. Ecotechnologies are based on the science of ecology and the consideration of the ecosystem as an integral part of any proposed human or societal interventions involving the natural environment. Ecotechnologies are dependent on the self-designing capabilities of ecosystems and nature. This focus on, and use of, biological species, communities, and ecosystems distinguishes ecotechnologies from the more conventional engineering technology approaches, which rely on devices and facilities to remove, transform, or contain pollutants, but which seldom consider integrative ecosystem-based approaches.

Combined with an understanding of the hydrological and biogeochemical processes, phytotechnologies can be used to increase plant biomass and diversity and to regulate nutri-

ents and water dynamics, thereby increasing ecosystem carrying capacity and enhancing the resilience and functionality of ecosystems. This can lead to significant improvements in water quality, enhanced biodiversity, improved agricultural production and potential bioenergy generation, as well as remediation of degraded ecosystems.

mixed species of vegetation can also lead to greater chances of success than the use of monocultures. Care should be taken not to introduce species of plants that are invasive or a nuisance. In cases where the spread of a plant is undesirable, the plants should be selected to prevent reproduction.



Phytotechnology Applications

Specific environmentally beneficial applications of phytotechnologies involve the use of plants to augment the capacity of ecosystems to absorb impacts; to prevent, reduce or remediate pollution; and to monitor and assess ecosystems health. Methods might use plants to break down or sequester pollutants (sometimes making useful products as an added benefit), or replace existing activities that pollute with ones that do not. Applications can also include the use of plants for water cycle and ecosystems restoration. Although the concept is not entirely new, this area is evolving and novel applications are continuing to emerge.

An understanding of the potential and limitations of phytotechnologies is crucial for their successful application. Limitations include insufficient knowledge and expertise regarding plant selection and the factors, which influence plant growth, as well as public and regulatory acceptance. Each application of phytotechnology involves site-specific considerations and should be evaluated on a case-by-case basis. The developers and proponents of phytotechnology systems must be able to demonstrate how phytotechnology will meet environmental performance objectives and minimise risk to human health.

The application of phytotechnology involves more than going to a site and planting seedlings, grass or some other type of plant. Phytotechnology is an in situ approach that requires careful consideration of site-specific characteristics. Native, non-agricultural plants are generally preferred for phytotechnology applications. In most applications, plants that are adapted to local conditions will have better chances of success than non-adapted plants. The use of

The effectiveness of phytotechnology applications depends on having both broad-based and expert input into their development, adoption and ongoing monitoring. Governments, the private sector and citizens must all be involved, and systems for collecting, synthesising and feeding back information and knowledge on phytotechnologies must be established and maintained. Issues and concerns must be addressed in a transparent, credible manner, and proactive strategies are required to ensure the responsible development and application of phytotechnologies.

Phytotechnologies could be separated into five major categories: integrated ecosystems management, prevention, control, remediation of polluted sites, restoration, and monitoring and assessment. **Integrated ecosystems management** focuses on augmenting the capacity of natural systems to absorb impacts. **Prevention** involves technologies that avoid the production and release of environmentally hazardous substances or alter human activities in ways that minimise damage to the environment; it encompasses product substitution or the redesign of an entire production process, rather than simply using new pieces of equipment. **Control** technologies render hazardous substances harmless before they enter the environment. **Remediation and restoration** technologies embody methods designed to recuperate and improve ecosystems that have declined due to naturally induced or anthropogenic effects. **Monitoring and assessment** technologies are used to monitor and assess the condition of the environment, including releases of pollutants and other natural or anthropogenic materials of a harmful nature. Next figure illustrates the broad application of phytotechnologies in addressing environmental requirements.

WATERSHED MANAGEMENT

Over a billion people worldwide lack access to adequate water, and close to two billion suffer the consequences of poor sanitation; millions of people die each year from contaminated water. Furthermore, water quality, expressed as secondary pollution and toxic algal blooms, continues to decline in aquatic ecosystems around the world. This decline is sobering evidence that the prevailing approach to catchment-scale water management does not guarantee sustainable water use. Technical approaches to pollution control, such as sewage treatment plants and regulation of hydrological processes for flood and drought control, are crucial but not sufficient. Purely technical controls, without understanding and consideration of biota dynamics, reflect a trial and error approach to water management rather than the implementation of a policy toward sustainable use of water resources.

A watershed planning and management strategy within a hydrologically-defined area provides a coordinating framework for water supply protection, pollution prevention and ecosystem preservation. Although watershed strategies vary, they should be based on ecohydrology, the integrated study of ecosystems and hydrological characteristics and processes and their combined potential to influence water dynamics and quality. Ecohydrology requires an understanding of the temporal and spatial patterns of catchment-scale water dynamics, which are determined by four fundamental components: climate, geomorphology, plant cover/biota dynamics and anthropogenic modifications. A more efficient approach to water quality and ecosystem integrity requires not only the reduction or elimination of pollution, but, in parallel, an augmentation of the effectiveness of potential tools to manage the dynamics of excess nutrients, pollutants, mineral and organic matter in the landscape. This can be done by reducing human impacts and by regulating the aquatic and terrestrial biota in the catchment. One of the most efficient ways to control biota dynamics is through the regulation of hydrological processes by:

- increasing watershed water retention through reforestation and restoration of land/water ecotones
- enhancing in-stream retention of water sediments and nutrients through river renaturation and wetland restoration
- amplifying biogeochemical cycles such as denitrification through wetland inundation.

Recent and ongoing research has greatly increased our understanding of hydrological dynamics, as well as the biotic and biogeochemical dynamics in freshwater ecosystems and land/water ecotones. The application of biotic processes can facilitate self-purification in aquatic ecosystems, significantly reduce the costs of water quality maintenance, and expand the repertoire of management tools which can be applied to freshwater resources.

Ecotones are transition areas between two adjacent ecological communities, for example, between aquatic and terrestrial ecosystems. Ecotones are crucial for protection of these ecosystems against anthropogenic impacts. The transition area has the same function for an aquatic ecosystem,

such as a lake, as a membrane has for a cell. Essentially, the ecotone functions as a phytotechnology by preventing, to a certain extent, the penetration of undesirable contaminants into the lake. Thus, it is crucial to preserve the shore ecotones around surface water bodies and wetlands in the watershed as part of an integrated ecosystems management strategy.

Non-point or diffuse pollutants in the environment inevitably flow toward surface water bodies, however the transition zone is usually able to transform and/or adsorb most pollutants entirely or partially, within a certain threshold. This can significantly reduce the potential for irreversible effects on the watershed as a whole. Ecotones serve not only as a buffer zone for protection against pollutants, but also as productive habitat for species present in adjacent ecosystems.

The restoration of wetland basins and ecotones through re-establishment of aquatic vegetation, as well as soil carbon restoration in riparian zones and uplands that may be cultivated, is another important element of an integrated strategy to address climate change.

The preservation of natural wetlands at the shoreline is crucial for maintaining aquatic ecosystem biodiversity and should be considered as part of an effective ecosystem management strategy based on phytotechnology. There are four major groups of natural wetlands:

- Fringe wetlands, which include salt marshes and lake-side marshes in which water typically flows in two opposite directions, influenced by lunar and/or storm tides.
- Riverine wetlands, which occupy floodplains, are usually characterised by water flowing in one direction.
- Depressional wetlands, such as prairie potholes, which usually receive much of their water from runoff and/or groundwater seepage rather than from surface water bodies, so that water residence times are longer.
- Peatlands also have long water residence times, but the accumulated peat creates a unique hydrologic regime that differs from the previous three types of wetlands.

Water quality improvement is a positive service attributed to wetlands that absorb and recycle nutrients from human settlements. The denitrification potential of wetlands is often surprisingly high. As much as 2,000 to 3,000 kg of nitrate-nitrogen can be denitrified per hectare of wetlands per year, depending on the hydraulic conditions. This is important for the protection of surface waters because a significant amount of nitrate is released by agricultural activities. As much as 100 kg nitrate-nitrogen per hectare may be found in the drainage water from intensive agriculture. Since the denitrification is accompanied by the oxidation of organic matter, this process also removes a significant amount of organic matter.

CONSTRUCTED WETLANDS

Recognition of the ability of wetlands to filter, absorb and metabolise suspended and dissolved matter has resulted in the fact that drainage of wetlands has ceased in many countries. In some cases, previously drained wetlands are now being restored. Furthermore, scientists and engineers are now working together to mimic these natural systems in order to contain and/or treat wastewaters and/or agricultural run-off. This has prompted the construction of artificial wetlands to cope

with the diffuse pollution originating from agriculture, septic tanks, and other sources. In the U.S., for example, legislation prohibits the drainage of wetlands unless another wetland of the same size is constructed elsewhere.

Construction of artificial wetlands is an attractive and cost-effective phytotechnology that can be used for controlling pollution originating from diffuse sources and for treating various types of wastewater. For example, constructed wetlands can be used to treat dairy farm wastewaters, mine water pollutants, textile wastewater, and pulp mill wastewater. Still, it is important to ensure that the wetlands themselves are not sources of potential pollutants, such as phosphorus.

Artificial wetlands are usually constructed so that water flows primarily over the sediment and through vegetation, or as vegetated submerged bed systems in which water flow is engineered for contact with plant roots. They are excavated with a shallow gradient in soils of low permeability (or lined with an impermeable barrier and then filled with an appropriate soil). They are then either planted or vegetated naturally. They usually comprise several cells that can operate in a series or in parallel, allowing flows to be redistributed for greater control and easier maintenance.

Various emergent macrophyte species can be used in constructed wetlands, including cattails, bulrushes, reeds, rushes, papyrus, and sedges. Submerged species can be applied in deep-water zones. Species that have been used for this purpose include coon tail or horn wart, redhead grass, widgeon grass, wild celery, and water milfoil.

Improving water quality through the use of floating macrophyte species is another phytotechnology application. For example, the use of different types of duckweed and water hyacinths has been applied as an alternative to waste stabilisation ponds. The inorganic nitrogen and phosphorus contained in wastewater and decomposed from organic pollutants by microorganisms are absorbed by the water hyacinths. The water hyacinths with microorganisms and organic materials attached or coagulated on root surfaces can then be harvested as feed for fish culture ponds and animal farms. However, use of water hyacinths requires strict control, as they easily become widely spread as a weed, which may get completely out of control.

Many heavy metals are concentrated and accumulated in water hyacinths from very low concentrations in water. However, the heavy metal enrichment in this plant varies with its aquatic habitat. Water hyacinths with high residual amounts of heavy metals cannot be used as fodder, which limits the application of this phytotechnology for treating water polluted by organic pollutants (i.e., mainly municipal wastewater). Care must be taken in disposing of the plant biomass, as it can contain high levels of potentially toxic substances.

Combining the use of artificial wetlands with waste stabilisation ponds and root zone plants is an attractive wastewater treatment method for developing countries, recreational areas adjacent to lake ecosystems, and areas with low population density. The reasons for this are:

- Wetlands can provide, through the use of filter media (i.e., sand, gravel or peat), a significant reduction of suspended matter from maturation pond effluent.

- Wetlands can buffer the pH value of the effluent from a waste stabilisation pond.

- Effluents from waste stabilisation ponds most often need a post-treatment polishing step and the use of wetlands offers an excellent cost-effective solution to this problem.

- The use of waste stabilisation ponds and wetlands, in combination, offers a higher level of certainty as an effective pollution abatement and aquatic ecosystems management strategy.

PHYTOREMEDIATION

Phytoremediation is the term that refers to the use of plants for cleaning up contaminants in soil, groundwater, surface water and air. The use of phytoremediation can be a non-polluting and cost-effective way to remove or stabilise toxic chemicals that might otherwise be leached out of the soil by rain to contaminate nearby watercourses. It is also a way of concentrating and harvesting valuable metals that are thinly dispersed in the ground, and offers an attractive option for the remediation of brownfield sites. Phytoremediation encompasses several methodologies, including:

- phytoextraction or phytoconcentration, where the contaminant is concentrated in the roots, stem and foliage of the plant

- phytodegradation, where plant enzymes help catalyse breakdown of the contaminant molecule

- rhizosphere biodegradation, where plant roots release nutrients to microorganisms which are active in biodegradation of the contaminant molecule

- volatilisation, where transpiration of organics, selenium and mercury run through leaves of the plant

- stabilisation, where the plant converts the contaminant into a form which is not bioavailable, or the plant prevents the spreading of a contaminant plume.

The principal application of phytoremediation is for lightly contaminated soils, sludges and waters where the material to be treated is at a shallow or medium depth and the area to be treated is large, so that agronomic techniques are economical and applicable for both planting and harvesting. In addition, the site owner must be prepared to accept a longer remediation period.

Plants used to decontaminate soils must do one or more of the following:

- take up contaminants from soil particles and/or soil liquid into their roots

- bind the contaminant into their root tissue, physically and/or chemically

- transport the contaminant from their roots into growing shoots

- prevent or inhibit the contaminant from leaching out of the soil.

The plants should not only accumulate, degrade or volatilise the contaminants, but should also grow quickly in a range of different conditions and lend themselves to easy harvesting. If the plants are left to die in situ, the contaminants will return to the soil. For complete removal of contaminants from an area, the plants must be cut and disposed of elsewhere in a non-polluting way.

Typically, researchers look for suitable phytoremediation properties among both cultivated and wild varieties of plants. If suitable wild species are not available, researchers can try to improve the effectiveness of phytoremediation by introducing different genetic varieties. Although phytoremediation has not been used extensively, it has many advantages:

- It is low cost in comparison to current “mechanical” methods for soil remediation.
- It is passive and solar.
- It is faster than natural attenuation.
- The amount of contaminated material going to landfills can be greatly reduced.
- Energy can be recovered from the controlled combustion of the harvested biomass.
- It is low impact and public acceptance of phytoremediation is expected to be high.
- A major barrier to the implementation of phytoremediation is that it is new and not fully developed. There is little regulatory experience with phytoremediation and it has to be considered on a site by site basis. Momentum for the use of phytoremediation as a cleanup technique is building, particularly in application niches where other technologies are less suitable or do not exist.

CLIMATE CHANGE

Although the primary source of anthropogenic carbon dioxide emissions is the use of fossil fuels, deforestation contributes significantly to the net increase of atmospheric carbon dioxide. Deforestation can be defined as the conversion of forest land to other land-use. This includes forest conversion for permanent land-use changes such as agriculture, as well as the development of permanent infrastructure, such as highways. Some of the other factors affecting GHG emissions include the harvest and use of wood commodities, and the establishment and operation of forest plantations. Forests also contain a high proportion of the world's biodiversity and as these areas are deforested, biodiversity is threatened. The identification of policies to reduce deforestation is an important element of an overall strategy to address both global climate change and biodiversity. Two important areas of activity related to this are afforestation and reforestation.

Afforestation is the planting of new forests on lands

which, historically, have not contained forests. Focusing on achieving goals which go beyond just carbon sequestration, such as environmental and land management goals, is likely to be the most successful approach to afforestation over the longer term.

Reforestation is the planting of forests on lands which have, historically, previously contained forests but which have been converted to some other use. Two elements of regeneration strategies that could increase carbon sequestration potential are species selection and density management. While current research is aimed at maximising the volumes of the commercial harvest, some results have shown that significant biomass gains can be achieved by modifying planting or spacing regimes. In addition to species selection and density management, increased planting instead of natural regeneration and seeding after harvesting can also increase carbon sequestration.

Another important climate change mitigation strategy to realise the potential of agricultural soil carbon sinks, including conservation practices on croplands (i.e., reduced or no tillage and reduced summer fallow), pasture management, conversion of marginal croplands to perennial grass and conservation of wetlands and riparian areas. Agricultural soil sequestration could offer crop producers greater revenue, and potentially lower input costs resulting from lower fuel use, as well as more efficient use of fertilizers. Encouragement of conservation practices on cropland, including no till and reduction in conventional summer fallow is potentially one of the more cost-effective strategies. The overall impact of agricultural soils conservation practices on the environment is a healthier, more productive soil that is less subject to wind or water erosion, and a more resilient, environmentally sustainable agro-ecosystem.

The application of phytotechnologies in the management of forests, agricultural land and wetlands represents an important strategy for climate change mitigation and adaptation. However, the optimum use of phytotechnologies leading to the establishment of more resilient ecosystems requires a better understanding of the physiology of plant species under different environmental conditions, as well as an understanding of the role of plant biomass and biodiversity in relation to energy flows and ecohydrology.

CONCEPT FOR THE DERIVATION OF TRIGGER VALUES FOR THE SOIL-PLANT UPTAKE

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INTRODUCTION

The Federal Soil Protection Act [Anonymus, 1998] has been put into practice by the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) of July 12th, 1999 [Anonymus, 1999a]. Precautionary values and trigger values as laid down in the Law are an important instrument to realise its requirements. Trigger values are related to various soil uses and objectives of protection, which are „human health“, „quality of food and feed“, and „leachate to groundwater“. Any procedure to derive trigger values for the objective „quality of food and feed“ has to consider the soil-plant transfer of chemicals for soils under agricultural use and household gardens. Thus, the production function of soil is taken into account.

The exact procedure to obtain trigger values for „quality of food and feed“ is laid down in the Federal Bulletin No. 161a [Anonymus, 1999b] and has to be followed when deriving justiciable values:

- consideration of maximum residue levels in/on plants
- quantitative description of soil-plant transfer and derivation of a maximum acceptable soil content
- plausibility check
- final stipulation of trigger values.

By these means, trigger values for „quality of food and feed“ have already been derived for some metal compounds, namely arsenic, lead, mercury and thallium. Beside metal compounds several organic substances are also of priority. So far, a trigger value has been defined for benzo(a)pyrene and an action value for PCBs.

It is within the scope of the presentation to give a summary on the methodology and results of trigger value derivation for some selected organic chemicals previously used as pesticides and of different data sizes with respect to the soil-plant transfer process.

METHODOLOGY

a) Objective of protection: quality of food

1. Step: Consideration of maximum residue levels in/on plants

Trigger values are calculated by inclusion of maximum residue levels (MRL-levels, „Rückstandshöchstmengenverordnung“ of 21.10.1999, modified on 20.11.2000) and ADI-values, respectively. In case these official values have not been derived for the compound under consideration a preliminary MRL'-value is assessed using N(L)OAEI-values and additionally applying a safety factor (SF_{toxicological} reference). In case none of the toxicologically relevant data is available the soil trigger value cannot be derived.

2. Step: quantitative description of soil-plant transfer and derivation of a maximum acceptable soil content

The soil-plant transfer coefficient is defined as the quotient of the substance content in the respective plant compartment (given in dry weight) and the soil content (also given in dry weight):

$$f_{\text{transfer (i)}} = \frac{C_{\text{plant (i)}} [\text{mg/kg dm}]}{C_{\text{soil}} [\text{mg/kg dm}]}$$

Since the soil-plant transfer depends on both soil and plant properties, ideally each food item and all representative soils should be tested. However, such a broad variety of experimental studies is not achievable and thus, the following assumptions and definitions were applied:

- The ideal data set is characterised by five soils and ten representative food items. As long as a heterogeneous data-

base is available with information, which is difficult to interpret, the five soils / ten food items database is considered to be the optimum. In case systematic studies are published, a data set characterised by three soils and six food items is considered to be sufficient.

- In case the optimal soil data set is not available a safety factor (SF_{soil}) is applied to the mean transfer coefficient for each food item.

- The experimentally determined transfer coefficients for the individual food items each are combined and a mean is calculated.

The maximum tolerable soil content is, in a first step, calculated separately for each tested food item by using one of the alternative equations depending on the availability of MRL- and ADI-value, respectively.

In case MRL-values are available the equation is: with:

$$\text{maximum tolerable soil content (i) [mg/kg dm]} = \frac{f_{\text{transfer (i)}} [1 - (\text{water content [\%]} / 100)]}{\text{HF} \times \text{MRL (i) [mg/kg ww]}}$$

i = vegetable food (*i*)

MRL = maximum residue level [mg/kg wet weight]

f_{transfer(i)} = mean of transfer coefficients for food item (*i*)

HF = hazard factor according to approach „toxicological hazard assessment of chemicals“ [Anonymus, 1999c]

In case no MRL-value is available the equation is:

$$\text{maximum tolerable soil content (i) [mg/kg dm]} = \frac{\text{ADI [mg/kg bw d]} \times 20 \text{ kg} \times \text{portion (i) in food basket}}{f_{\text{transfer (i)}} [1 - (\text{water content [\%]} / 100)] \times \text{daily intake (i) [mg/kg]}}$$

where MRL' is:

$$\text{MRL' (i) [mg/kg]} =$$

$$\frac{\text{ADI [mg/kg bw d]} \times 20 \text{ kg} \times \text{portion (i) in food basket}}{\text{daily intake (i) [mg/kg]}}$$

with:

ADI = acceptable daily intake

20 kg = reference for daily intake: girl, 4-6 years of age, sensitive subgroup, weight 20 kg

The finally proposed maximum tolerable soil content, which is the basis for a plausibility check and expert-judgment, is identical with the lowest value out of the ensemble of calculated maximum tolerable soil contents for the individual food items. In case not all of the ten food items have been tested, again safety factors (SF_{food item}) are applied.

The finally proposed maximum tolerable soil content is multiplied with a so called „hazard factor“ (HF). Maximum

§ 8 Federal Soil Protection Act:

Precautionary values: „soil values which, if exceeded, shall normally mean there is reason to suspect that a harmful soil change exists, taking geogenic or wide-spread, settlement-related pollutant concentrations into account“.

Trigger values: „values which, if exceeded, shall mean that investigation with respect to the individual case in question is required, taking the relevant soil use into account, to determine whether a harmful soil change or site contamination exists.“

residue levels are derived as precautionary values. Food with residues below these levels should not cause adverse health effects for all population groups including sensitive subgroups such as children. However, a maximum tolerable soil content – in the sense of a trigger value - does not reflect the precautionary principle but the avoidance of hazards to human health. Thus, a hazard factor is added. The use of such a „hazard factor“ is in accordance with the derivation of soil trigger values for the objective of protection „human health, direct soil contact“ as published in the Federal Bulletin No. 161a.

3. Step: plausibility check and

4. Step: final stipulation of trigger values

The finally calculated maximum tolerable soil content, which has been multiplied with appropriate safety factors and the hazard factor is subjected to a plausibility check. The check comprises – among others – a comparison with background values and precautionary values in order to make the trigger values operable. Finally, the suggested

studies to small-scale laboratory studies. Consequently, the studies yield contradictory results for the degree of soil-plant transfer, the contribution by different exposure pathways, target organs and differentiation between HCH-isomers.

It was concluded that there is a principle need to derive trigger values for soil-plant uptake. The acquisition and evaluation of further homogeneous data sets in so-far unpublished or “grey” literature is recommended. Additionally, data selection criteria should be developed and applied to the entire data set. In particular the latter needs the implementation of an ad-hoc working group for consensus finding.

HEXACHLOROBENZENE

Homogeneous results on small-scaled laboratory studies are available. Though data from field studies is preferred over laboratory studies, maximum tolerable soil contents are derived exemplarily. The soil-plant transfer factors are given in Table 1:

Food	Study design	Quality of study	Transfer factor ¹
Oat, roots	desiccator, 1 soil	Low	36
Cress	desiccator, 1 soil	Low	105
Corn, roots	desiccator, 1 soil	Low	53
Rape, roots	desiccator, 1 soil	Low	152
Carrots	desiccator, 1 soil	Low	2250
Salat, roots	desiccator, 1 soil	Low	1230

triggers are stipulated in the course of a moderated round table discussion including expert judgement.

b) Objective of protection: quality of feed

For the derivation of maximum tolerable soil contents for the objective of protection „quality of feed“ the procedure as laid down in the Federal Bulletin No. 161a is followed:

- grassland and soil under agricultural use (for maize) are treated identically.

- The legal basis for maximum tolerable plant levels is Directive (29/99/EEC) as well as the German „Futtermittelverordnung“

- The Directive (29/99/EEC) gives maximum tolerable plant levels for aldrin, DDT, HCB, HCHs and dioxins without differentiating between feed items.

- For other than these compounds or compound groups the maximum tolerable soil content currently cannot be derived.

CALCULATION OF THE MAXIMUM TOLERABLE SOIL CONTENT FOR SELECTED COMPOUNDS

Hexachlorocyclohexane

For hexachlorocyclohexane comprehensive and numerous data sets exist on soil-plant-transfer studies. However, these studies are heterogeneous with respect to intention and design which ranges from using soils from contaminated sites to spiked soils and from outdoor field

¹ Safety factor (SF_{soil}) of 5 included because of information from one soil only available

Table 1: Soil-plant transfer factors for HCB derived from laboratory studies

In order to follow a worst-case approach the highest transfer of 2250 is used to calculate the maximum tolerable soil content:

Maximum tolerable soil content (carrots) =

$$5,5 \times 0,05 / 2250 [1 - 88,2/100] = 1,1 \text{ ug/kg}$$

MRL-value	=	0,05 [mg/kg dm]
hazard factor (HF)	=	5,5
water content	=	88,2%

A comparison of the calculated maximum tolerable soil content with the stipulated trigger value for the path soil-human being (playground) as well as with background values shows comparability with background values (Table 2).

It was concluded that there is principle need to derive a trigger value for the path soil-plant uptake. Calculated maximum tolerable contents derived from laboratory studies are in the range of background values. Such a result can be explained by a principally observable systematic over-

Background value (grassland)	0,2 – 12 ug/kg
Background value (agricultural soil)	0,5 – 13 ug/kg
Trigger value (path soil – human being, playground)	4 mg/kg
Calculated maximum tolerable soil content (soil – plant uptake)	1,1 ug/kg

Table 2: Plausibility check: comparison with trigger and background values

estimation of the chemicals transfer in laboratory studies using desiccators. Thus, for the derivation of justifiable and operable trigger values, results from field and lysimeter studies, respectively, are needed.

DDT

Because of the long-time use of the pesticide DDT, comprehensive studies, in particular field studies, are available. Again, for the derivation of the maximum tolerable soil content safety factors are used depending on the number of soils and food items tested. Table 3 presents input information, measured transfer factors and calculated maximum tolerable soil contents.

It was concluded that there is principle need to derive a trigger value for the path soil – plant for DDT. As for hexachlorocyclohexane, an ad-hoc task force will be implemented for the final value stipulation.

PENTACHLOROPHENOL

Due to the degradation potential of pentachlorophenol, the transfer factors obtained on the basis of short-term laboratory studies are not comparable to long-term studies. At soil contents below toxicity to micro-organisms, metabolism under aerobic conditions occurs. The transfer factor of PCP is lower than 0,01 in alkaline soils, and even lower in acid soils due to reduced bioavailability.

Food	Study design	Quality of study	Transfer factor	Maximum tolerable soil content [mg/kg] 4, 5
carrots	field, 5 soils ²	Relatively high	0,6 ¹	2,3
beets	field, 1 soil ³	Relatively high	0,05	6,7
potatoes	field, 1 soil	Relatively high	0,2	0,7
radish	field, 1 soil	Relatively high	0,35	1,3
rapeseed	field, > 5 soils	Very high	0,3 ¹	0,7

Table 3: Soil-plant transfer factors and maximum tolerable soil contents for DDT derived from field studies

¹ mean

² safety factor = 1 (5 soils tested)

³ safety factor soil = 5 (1 soil tested)

⁴ hazard factor HF = 10

⁵ safety factor food = 3 (5 food items tested)

As for hexachlorobenzene, the calculated maximum tolerable soil content is compared with the stipulated trigger value for the path soil – human being (playground) as well as with several sets of monitoring data. The calculated tolerable contents for the path soil – plant are in the range of monitoring data but far below the trigger value for the path soil – human being.

Monitoring data (industrial area)	0,16 – 0,25 mg/kg
Monitoring data (agricultural soils)	0,03 – 1,5 mg/kg
Trigger value (path soil – human being, playground)	40 mg/kg
Calculated maximum tolerable soil content (soil – plant uptake)	0,7 mg/kg

Table 4: Plausibility check: comparison with trigger values and monitoring data

From these observations it was concluded that there is no need to derive trigger values.

DISCUSSION

A comparison of soil trigger values derived for various objectives of protection (e.g. „human health – direct soil contact“ versus „quality of food and feed“ versus „groundwater protection“) yields very low values for the soil-plant transfer path. From the discrepancies it can be concluded:

- Due to possible accumulation in the food chain the soil-plant transfer path is a sensible one and has to be considered carefully.

- The derivation of maximum tolerable soil contents using the suggested procedure and assumptions leads to trigger values, which are lower than those obtained for the path „direct soil contact“, and to values in the range of soil background contents.

- A uniform experimental design should be used as basis to obtain comparable transfer coefficients for all substances under discussion. This is not the case at present, and thus an overestimation of the soil-plant transfer might occur.

- Recent studies are heterogeneous in respect of design of the study (field testing – lysimeter – laboratory study...),

mode of soil contamination, investigated and published soil data, extraction methods and analytical procedures and missing inclusion of wet and dry deposition.

CONCLUSIONS

The procedure to derive soil trigger values for the objective of protection „quality of food and feed“ is conclusive and presents a pragmatic approach. The approach differs in respect to the procedure selected for metals and metal compounds. Though 10 representative food items are suggested for inclusion in the procedure, „special cases“ in respect to a selective plant uptake (such as spinach) should be considered additionally. In case of an insufficient database, safety factors are applied. The suggested factors can be interpreted as „signals“ for further discussions in ad-hoc working groups, and for optimisation or mutually agreed interpretation of the current data set. For organic chemicals the airborne impact, i.e. wet or dry deposition, should additionally be taken into account. It is a challenging task to integrate all exposure pathways and a jointly designed approach should be elaborated as soon as possible.

Several substances and groups of substances were identified

for which need exists to derive soil trigger values for the objective of protection „quality of food and feed“. These chemicals are: aldrin, PAHs, DDT, hexachlorobenzene, HCHs, and PCBs.

Literature

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PLANT SPECIES MONITORING FOR PHYTOREMEDIATION OF PESTICIDE-CONTAMINATED SOIL

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ABSTRACT

Unsafe and obsolete pesticides are hazards for human health and a threat to the environment. It is an important and widespread problem in Kazakhstan. Unfortunately, many places where these pesticides were stored are in disrepair or have been destroyed. Many pesticides of unknown origin are stored open to the air where they pollute the environment. Phytoremediation is one potential method for reducing risk from these pesticides. Genetic heterogeneity of plant populations of wild and weedy species growing on pesticide-contaminated soil provides a source of plant species tolerant to these conditions. These plant species may be useful for phytoremediation applications.

MATERIALS AND METHODS

Many storehouses for agricultural pesticides were destroyed in Kazakhstan during 1989-1991. This occurred during a period of restructuring of the Agriculture Ministry when financing was not available to maintain these facilities. In the Republic of Kazakhstan there are approximately 1884 pesticide storehouses with 411 in an emergency condition. An estimated five hundred seventy-four (574) tons of pesticides and fifty (50) thousand containers have accumulated which are stored open to the air where they pollute the environment. These former pesticide storage sites are "hotspots" that represent an ecological danger for the country.

The locations for our research are three destroyed pesticide storehouses and the land surrounding these facilities. They are located near the largest city in Kazakhstan, Almaty. The first site or hot point is a former agrochemical storehouse covering an area of 80 m². At the second hot point the contaminated zone represents the destroyed base of a former pesticide storage building covering an area of 60 m². The third hot point is represented by a concrete pad located in a wooded area ringed by trees in the genera *Acer* and *Ulmus*. The site covers an area 100 m².

The identity and concentration of pesticides at the contaminated sites has not been established. To characterize residual amounts of pesticides in the soil, sampling was conducted according to accepted engineering specifications and state standards for the Republic of Kazakhstan [2, 3]. Soil samples were taken from the top 50 cm of soil using a shovel that was decontaminated with detergent between samples. Each sample was mixed and a composite of 400-500 grams was saved for analysis. Seventeen (17) total soil samples were taken from the three contaminated sites. Soil

was initially stored in paper bags, then transferred to labeled plastic bags and transported to the laboratory in coolers. Soil samples were stored frozen until analysis.

Soil extraction methods: Ten (10) grams of soil were subsampled from each initial sample after mixing the sample thoroughly. The soil was transferred to a 250 ml conic flask. Twenty (20) ml of distilled water was added to the flask. The flask was sealed and stored for one day. Ten (10) ml of acetone and forty (40) ml of hexane were added to the wet soil. The mixture was vigorously stirred on a shaker for one (1) hour. The contents of the flask was transferred to centrifuge tubes and centrifuged for 15 minutes at (2000 rpm). The supernatant was decanted in a liquid phase to a 500 ml separatory funnel. Soil in the centrifuge tubes was washed with ten (10) ml hexane and transferred to the separatory funnel. Thirty (30) ml water was added to the liquid phase in the separatory funnel. The contents of the separatory funnel were stirred manually for 3 minutes. The water—acetone layer was separated from the organic layer and extracted three (3) times with ten (10) ml hexane. The combined hexane extracts were concentrated with a rotor evaporator to a volume of 5-10 ml.

Cleanup of extracts by sulfuric acid: The concentrated hexane extract was transferred to a separatory funnel and 5-10 ml of concentrated sulfuric acid was added and stirred for two (2) minutes. The lower sulfuric acid layer was separated and the operation was repeated until the sulfuric acid layer was no longer colored. The organic layer was washed by adding 5 % sodium bicarbonate solution, then adding water. The solution was then dewatered using sodium sulphate. The dried hexane solution was evaporated at room temperature to a volume of 3-5 ml.

Gas chromatography: Organochlorine pesticides were quantified by gas chromatography (GC) using an electronic-capture detector (ECD). Details of the chromatography methods will be described elsewhere.

Identification of plant species and description of plant community structure at the hot points: Vegetation surveys were used to select plants which may be capable of accumulating or degrading pesticides using accepted engineering specifications and State standards for the Republic of Kazakhstan [2, 3]. We studied the plant community structure within a radius of 100 – 300 meters of the center of each contaminated site. The distribution and taxonomic identification of plant species used the Tahtadjan technique [4] taking into account main morphological attributes and structural parameters of plant communities including: aspect, specific structure, area cover, plant distribution, abundance, plant community adaptations, frequency, phenological stage of development and vigor of each separate plant species.

RESULTS

Preliminary results from soil analyses at three former pesticide storage sites show that the field sites are contaminated with metabolites of DDT and isomers of HCH (Table 1). The maximum concentrations observed from all sites were as follows: 4,4-DDE - 2733,0 ug/kg, 2,4-DDD - 43,0, ug/kg, 4,4 DDD -295,0 ug/kg, 4,4 DDT - 1650,0 ug/kg, beta-HCH - 330,5 ug/kg, gamma-HCH - 56,5 ug/kg, and

alpha-HCH -112,0 ug/kg. The main contaminants occurring in excess of the Maximum Allowable Concentrations (MAC) were beta-HCH, exceeding the (MAC) by 230,0 ug/kg of soil, alpha-HCH exceeding the MAC by 112 ug/kg of soil, and 4,4-DDD, exceeding the MAC by 295 ug/kg of soil. The presence of high concentrations of DDT metabolites such as DDE indicates the widespread use or storage of DDT although the application of DDT was terminated in the Soviet Union in 1971. These data demonstrate the persistence of metabolites of DDT and isomers of HCH. Of special concern is the presence of γ -HCH, 4,4-DDD, and 2,4-DDD at the field sites since there are no allowable concentrations of these in soil. The level of alpha-HCH varied from < 1,0 to 112,0 ug/kg of soil, 4,4 DDD varied from 1,0 to 295,0 ug/kg of soil, and 2,4-DDD varied from 6,5 ug/kg to 43,0 ug/kg of soil. These results are disturbing and testify to ecological disaster present at these locations and the potential health danger they pose to neighboring settlements.

Plant community structure at the contaminated sites:

It is known that each plant species has adaptations that contribute to the functioning of a healthy ecosystem. Plant species diversity at the centers of infection and in the surrounding zone of influence included more than 100 species of flowering plants (not including vernal ephemeral species). Species from 19 angiosperm families were identified. The most widespread and predominant species were wild and weedy annuals in the division Magnoliophyta and classes Magnoliopsida and Liliopsida or Mono-cotyledoneae. In the central zone of the hot spots, annual species were primarily from the following families: Brassicaceae (*Descurainia sophia*), Cannabinaceae (*Cannabis ruderalis*), Polygonaceae (*Polygonum aviculare*), Chenopodiaceae (*Atriplex tatarica*, *Chenopodium album*), Amaranthaceae (*Amaranthus retroflexus*), Asteraceae (*Artemisia annua*, *Ambrosia artemisiifolia*, *Erigeron canadensis*); Biannual species were primarily from Asteraceae (*Onopordon acanthium*), Brassicaceae (*Barbarea vulgaris*) and perennial species of plants were from Fabaceae (*Vecsibia alopecuroides*) and Poaceae (*Poa bulbosa*, *Cynadon dactylon*). Woody plant forms were represented by isolated individual seedlings of small bushes or trees up to 120 cm in height. *Ulmus pumila* was the primary tree species observed.

Preliminary results of plant community analysis of vegetative cover from the three locations revealed promising pesticide tolerant plant species that warrant further investigation (Table 2). In June and July, the first hot point, was dominated by *Erigeron canadensis*, *Barbarea vulgaris*, *Onopordon acanthium*, *Descurainia sophia*, *Chenopodium album*, *Artemisia annua*, *Vecsibia alopecuroides*. The vegetative cover at the second hot point differed in diversity and variety compared to the first site. The second site included species from the following ecosystem types: steppe (*Leonorus incanus*, *Artemisia siversiana*, etc.), foothill (*Rosa canina*, *Origanum vulgare*), desert (*Eremopyrum orientale*) and interzonal meadow (*Mentha arvensis*, *Trifolium pretense*, etc.). Several potential "hyperaccumulating" species from this site included *Kochia prostrata*, *Erigeron canadensis*, *Camphorosma lessingii*, and *Chenopodium*

Sample	Alpha-HCH	Beta-HCH	Gamma-HCH	4,4-DDE	2,4-DDD	4,4-DDD	4,4-DDT
MAC	0	100	100	100	0	0	100
First site 1	21,0	182,0	10,0	15,5	0	4,5	15,0
First site 2	30,5	180,5	18,0	20,5	0	4,5	29,5
First site 3	112,0	269,0	56,5	55,5	0	30,5	206,0
First site 4	52,5	146,0	21,5	71,5	0	15,0	38,5
Second site 1	5,0	166,0	2,0	193,0	8,5	91,0	300,0
Second site 2	9,5	146,0	1,5	2160,0	43,0	60,5	194,0
Second site 3	15,5	330,5	3,5	204,0	28,5	71,0	382,0
Second site 4	10,0	154,0	2,0	2733,0	0	295,0	1650,0
Second site 5	13,0	234,0	2,5	2627,0	0	139,0	941,0
Second site 6	5,5	177,0	1,5	2107,0	0	39,5	220,5
Third site 1	< 1,0	111,5	< 1,0	180,0	6,5	7,5	79,5
Third site 2	2,5	120,0	< 1,0	56,5	0	0	13,0
Third site 3	3,0	132,5	7,0	460,0	7,0	16,5	112,0
Third site 4	1,0	114,0	< 1,0	98,0	0	4,0	37,5

Table 1: Concentration of pesticides in 17 soil samples from three former pesticide storage sites. Concentrations are given in ug/kg of soil. Maximum concentrations are indicated in bold type. MAC denotes the maximum acceptable concentration in soil by.

botris. This needs to be confirmed by further analyses of plant uptake of pesticides. In northern part of the second site, there was algae growing on the soil surface, however in October, there were numerous individuals of *Trifolium repens* and single individuals of *Cichorium intybus* and *Medicago sativa* in the same area. The center of the third hot point is a concrete slab located within a wooded area. The dominant tree species are *Necundo* sp. and *Ulmus pumila*. The most promising pesticide tolerant species at this site include *Onopordon acanthium*, *Malva neglecta*,

Chenopodium album, *Descurainia Sophia*. These species occur in openings among the trees and in places where the concrete foundation has been cracked or disturbed.

From more than 100 plant species that were identified from the three sites, only 12 species dominated in the center of the contamination zones. These species deserve further investigation for their potential to remediate pesticide contaminated sites. The center of the contamination zone has suffered the greatest damage to the ecosystem and disruption to normal plant community structure. This is also observed by the effect on phenological development and plant vigor.

This preliminary study has shown that these former pesticide storage sites have soil contaminated by metabolites of DDT and isomers of HCH. These contaminants present a threat to the local environment. Observations of plant diversity at these sites show that each site has a specific plant community structure. The results from this preliminary soil characterization and description of plant diversity will be investigated further to select plant species for their ability to hyperaccumulate or degrade pesticides. Further monitoring and characterization of these contaminated sites is also planned.

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Plant species	Family
First point	
<i>Descurainia sophia</i>	Brassicaceae
<i>Erigeron canadensis</i>	Asteraceae
<i>Chenopodium album</i>	Chenopodiaceae
<i>Onopordon acanthium</i>	Asteraceae
<i>Polygonum aviculare</i>	Polygonaceae
Second point	
<i>Kochia prostrata</i>	Chenopodiaceae
<i>Polygonum _viculare</i>	Polygonaceae
<i>Camphorosma lessingii</i>	Chenopodiaceae
<i>Origanum vulgare</i>	Lamiaceae
<i>Cichorium intybus</i>	Asteraceae
<i>Artemisia siversiana</i>	Asteraceae
Third point	
<i>Onopordon acanthium</i>	Asteraceae
<i>Malva neglecta</i>	Malvaceae
<i>Chenopodium album</i>	Chenopodiaceae
<i>Ambrosia artemisifolia</i>	Asteraceae
<i>Descurainia sophia</i>	Brassicaceae

Table 2: Dominant plant species occurring at the center of contamination at three pesticide contaminated sites.

THE POTENTIAL FOR PHYTOREMEDIATION OF DDT: GREENHOUSE STUDIES

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INTRODUCTION

A large number of sites across the world are contaminated with organochlorine pesticides. In the last decade, the search for alternatives to common, and typically very expensive, environmental remediation technologies has been intensifying. Consequently, there has been increasing interest in the development of 'green' or plant-based technologies to remediate these contaminated sites. Phytoremediation, which involves growing plants in situ to take advantage of their natural ability to accumulate and/or degrade contaminants, is a novel treatment that may be highly applicable to many contaminated sites. The term 'phytoremediation' actually refers to a number of different technologies including phytoextraction, phytodegradation, phytostabilization, phytotransformation, and phytovolatilization (Glass 1998). As the terms suggest, specific plants can be used to extract, degrade, stabilize, transform and/or volatilize contaminants from a number of different matrices including soils, water, sediments, and sludges. The root systems of plants provide a natural adsorptive net, as well as an effective environment for beneficial microbes to inhabit.

The need for cost-effective solutions to dealing with organochlorine-contaminated sites worldwide presents an ideal opportunity for applied phytoremediation research projects, despite the fact that many researchers have dismissed the possibility of phytoremediating contaminants that are highly hydrophobic in nature (i.e. those with a K_{ow} generally >3.5) (e.g. Bell & Failey 1991; Schnoor et al. 1995). The insecticide, DDT ($C_{14}H_9Cl_5$), has a log K_{ow} of 6.0, and is classified as a persistent organic insecticide with known adverse toxicological effects (CCME 1991; Grasman et al. 1998). Its use has been banned in North America since about 1970, but as of 2000 was still used in more than 30 countries. In the environment, DDT can be degraded microbiologically or abiotically to DDD or DDE, although when measured in the environment, it is common to report the sum of all isomers of DDT, DDE, and DDD as SDDT (Aislabie & Lloyd-Jones 1995; Corona-Cuz et al. 1999). Given the number of sites previously and currently being contaminated with SDDT, this insecticide can be considered a worthwhile candidate for phytoremediation. Previous studies have examined phytoremediation of DDT and/or DDD and DDE, but these have typically involved cell cultures or freshly-spiked soil, conditions which are far removed from the natural environment in which phytoremediation technology would be implemented, or weathered soil that has already

been significantly degraded to DDE (Arjmand & Sanderman 1985; White 2000, 2001, 2002).

During routine site assessment work at an abandoned Long Range Aid to Navigation (LORAN) site in northwestern Canada, a number of plant species were found to be flourishing in DDT-contaminated soils (ESG 2000). During active operation of the site between 1948-1950, workers encountered a severe mosquito problem, and in response liberally applied DDT as indicated by this station diary entry for July 5, 1948:

'Whole of the camp area is sprayed at least once per day to control pests. Inside of window sills have strips of cloth soaked in DDT solution tacked on to aid in pest control. Solution added to cloth daily to maintain moisture content...'

Soils collected directly from this site were used in the present study to examine the potential for phytoremediation of weathered SDDT. An overview of the work is presented here; details are presented in Lunney et al. (in press).

METHODS

Experimental

a) Soil

Treatments consisted of soils contaminated with high (~3700 ppb) and low (~150 ppb) levels of SDDT. Interestingly, due to low ambient temperatures, the DDT-contaminated soil mixture collected from the Kittigazuit site in northwestern Canada had degraded very little since its application. The ratio of isomers and metabolites was hence similar to that found in the original technical grade DDT (77.1% 4,4'-DDT, 14.9% 2,4-DDT, 4.0% 4,4'-DDE, 0.1% 2,4-DDE, 0.3% 4,4'-DDD, 0.1% 2,4-DDD and 3.5% unidentified compounds) sprayed on the site over 50 years ago.

b) Plants

Plant species (rye grass – *Lolium multiflorum*; tall fescue – *Festuca arundinacea* Schreb.; alfalfa – *Medicago sativa*; zucchini – *Cucurbita pepo* L.; and pumpkin – *Cucurbita pepo* cv Howden) were chosen from the literature as potentially effective phytoremediators on the basis of large root system, release of root exudates, and association with microbial communities. In order to limit volatilization, and hence focus on phytoextraction of SDDT by the plants, all planting trays were covered with laboratory parafilm.

Planting trays were perforated and bottom-watered as needed, and plant heights were measured on a regular basis. Plants were harvested when plots of height data showed a decline in growth rate, which occurred approximately 50 days after planting.

Zucchini, tall fescue, rye grass, and alfalfa were harvested by removing the entire plant from the soil, and subsequently separating plant roots and shoots. Pumpkin plants were similarly harvested by separating roots and shoots, and subsequently subdividing shoots for a more detailed analysis of translocation in the above ground portion of the plant. The shoot fractions for pumpkin included the lower stem, defined as the above ground portion of the plant below the oldest

leaf; the upper stem above the oldest leaf; the leaves, and the flowers. All plant samples were washed thoroughly under running water to remove any soil particles present. The fresh weights and lengths of all plant samples were recorded.

Analytical

All soils and plants were analyzed at the Analytical Services Unit (ASU) at Queen's University in Kingston, Ontario. The use of standardized analytical methods is extremely important to allow for comparison of results between different laboratories in different regions and countries. Hence, detailed analytical techniques used are provided here.

a) Soils

For Quality Assurance/Quality Control, all analytical runs included a blank, control and sample duplicate. Blanks were prepared with approximately 40 g of anhydrous sodium sulphate and 20 g of Ottawa sand, then spiked with 100 mL of a surrogate, decachlorobiphenyl (DCBP). Controls were prepared as above, but were additionally spiked with 50 mL of an organochlorine pesticide mix prepared at ASU. Soil samples from the greenhouse were prepared in the same way as the blanks with anhydrous sodium sulphate, Ottawa sand, and DCBP. All samples were corrected for surrogate recovery. For each soil sample, 10 g (± 0.5 g) of wet soil was weighed into thimbles. A sub-sample of each sample was dried for at least 24 hours at 100 °C and then weighed for moisture determination.

Samples were extracted in a soxhlet apparatus for 4-6 hours with 250 mL of methylene chloride (Fisher Scientific, D151-4). The extract was concentrated by roto-evaporation to 1 mL and the solvent exchanged to hexanes (Fisher Scientific H303-4) using a Büchi Rotavapor R-114. The extract was applied to a Florisil column, and diluted with hexanes to 10 mL. A fraction of the eluant was transferred to a vial for analysis by gas chromatography/electron capture detector (GC/ECD) to determine the composition and quantity of SDDT in soils. Concentrations of SDDT in soils were calculated from SDDT standards run with each batch of samples. GC/ECD analysis used an Agilent 6890 gas chromatograph and electron capture detector. Results obtained for 4,4'-DDT, 2,4-DDT, 4,4'-DDE, 2,4-DDE, 4,4'-DDD, and 2,4-DDD were expressed as nanograms of pesticide per gram dry weight of soil (ng/g). The analytical detection limit for this method was 10 ng/g for all of the DDT, DDE, and DDD compounds. All blanks were below sample detection limits (<10 ng/g), and controls were within acceptable limits of the control target as set by EPA Method 8250A (US EPA 1994). The coefficient of variation for duplicates ranged from 2.9% to 11.8%. Surrogate recovery was between 70-120%.

b) Plants

Plants were air-dried and weighed for moisture determination. Dried plants were combined with anhydrous sodium sulphate and ground to a fine powder with a mortar and pestle. For Quality Assurance/Quality Control, all analytical runs included a blank, control, and a sample duplicate. Common lawn grass from a residential area in Kingston, Ontario was ground and used for blanks and controls.

Blanks were prepared with approximately 1-2 g of lawn grass, 40 g of anhydrous sodium sulphate and 20 g of Ottawa sand, and then spiked with 100 mL of a surrogate, DCBP. Plant samples from the greenhouse were prepared in the same way. Controls were also prepared in the same way, but were additionally spiked with 50 mL of the same prepared organochlorine pesticide mix used for the control soils. All samples were corrected for surrogate recovery.

Samples were extracted in a soxhlet apparatus for 4-6 hours using 250 mL of methylene chloride. The extract was concentrated to approximately 10 mL by roto-evaporation. The concentrated extract was then filtered through a 0.45 mm syringe filter into a 50 mL vial and was rinsed thoroughly with methylene chloride. The filtered extract was then concentrated down to 1 mL by blowing down with nitrogen gas. This was run through an SSI 222C HPLC pump and a Chromaflex gel permeation cleanup column to separate pesticides from plant lipids. The lipid fraction was evaporated to determine lipid content of the plants. The pesticide fraction collected from the column was solvent exchanged with hexanes and concentrated to 1 mL by roto-evaporation. The concentrated extract was applied to a Florisil column and was flushed through with 10 mL of hexanes and then concentrated down to 0.5 mL by blowing down with nitrogen gas. A sub-sample was transferred to a vial for analysis by gas chromatography/electron capture detector (GC/ECD) to determine the composition and quantity of SDDT in the plants. Results obtained for 4,4'-DDT, 2,4-DDT, 4,4'-DDE, 2,4-DDE, 4,4'-DDD, and 2,4-DDD were expressed as nanograms of pesticide per gram dry weight of plant (ng/g). The analytical detection limits for this method varied between samples for all of the DDT, DDE, DDD compounds; the detection limits ranged from 1.0 ng/g, up to 50 ng/g for one sample. The higher detection limits were for plant samples <0.5 g by dry weight. All blanks were below sample detection limits (<5.0 ng/g). Controls were within acceptable limits of the control target as set by EPA Method 8250A (US EPA 1994).

Data Analysis

Bioaccumulation factors (BAFs) were calculated as $[\text{SDDT}]/\text{root or shoot} / [\text{SDDT}]/\text{soil}$ to compare the relative abilities of the five plant species to transport SDDT to the roots and the shoots. Translocation factors (TLFs) were calculated as $[\text{SDDT}]/\text{shoot} / [\text{SDDT}]/\text{root}$ to reflect the amount of contaminant that is transported to the shoots with respect to the amount that is in the roots.

Principal Components Analysis (PCA), a multivariate statistical technique, was used to elucidate differences in the pesticide composition of soil and plant samples using the program SYSTAT 8.0. Where samples had levels of DDT, DDD, or DDE compounds below detection limits, the concentration was assigned a value of half the detection limit (e.g. <1.0 ng/g = 0.5 ng/g).

RESULTS & DISCUSSION

Pumpkin and zucchini plants in the high SDDT soil treatment took up the highest concentrations of SDDT. Pumpkin accumulated 2393 ng/g in the roots and 4262 ng/g in the

shoots. Zucchini accumulated 2273 ng/g in the roots and 2991 ng/g in the shoots. Similarly, the highest root BAFs were for pumpkin and zucchini in the low SDDT-contaminated soil at values of 2.0 and 3.3, respectively. For the shoots, all BAFs were <1.0 except for pumpkin in both high and low SDDT-contaminated soil, which had values of 1.2 and 2.4, respectively, and zucchini in the low SDDT-contaminated soil, which had a shoot BAF of 1.5. All TLFs were below 1.0 except for pumpkin in the high and low SDDT-contaminated soil with TLFs of 1.8 and 1.2, respectively, and zucchini in the high SDDT-contaminated soil, with a TLF of 1.3.

The absolute amounts of SDDT accumulated in the roots and shoots of all study species and shoot compartments of pumpkin were determined by multiplying the concentration of SDDT accumulated in each plant compartment by its respective dry weight. In comparison to shoots, roots comprised a much lower percentage of total plant biomass; roots comprised as low as 7.1%, and the shoots comprised as much as 92.9% of the total plant biomass. In comparison to other plant species in this study, the shoots of pumpkin and zucchini plants, both members of the Cucurbita, comprised approximately 15–40% more of the total biomass. Hence, these were the only two plants to accumulate large concentrations of absolute amounts of SDDT in the shoots with 57536 ng and 35277 ng, respectively. For the whole plant, pumpkin again accumulated the highest amount of SDDT (59055 ng).

The percent distribution of absolute amounts of SDDT was further compartmentalized in pumpkin plants. In both the low and the high SDDT soil treatments, approximately 10% of the contaminant was in the root, and the majority of the contaminant (50–60%) was concentrated in the upper stem of the plant. The leaves contained 2–20%, while the flowers contained only 3–12%. It is a significant observation that ~90% of the SDDT extracted into the plant ended up in the ground above, and hence easily harvestable, portion of the plant. This is important for the ultimate application of phytoremediation at a contaminated site.

Principal component analysis showed that there was little or no preferential translocation or chemical transformation of SDDT compounds in most plant tissues, except in high alfalfa shoots and pumpkin flowers, where there was a higher proportion of 2,4-DDD. This apparent lack of transformation of SDDT compounds in most plant tissues, may allow for a faster rate of movement of the contaminant through the plant, and subsequently contribute to the accumulation of higher amounts of SDDT in the above ground biomass.

CONCLUSIONS

Soils were covered in this study, thereby verifying that the major SDDT burden in plants is due to the movement of contaminant molecules across the roots and translocation into the shoots. In a real world application, phytoremediation would not be carried out under such controlled conditions, and therefore (due to volatilization and subsequent foliar deposition), plants would be expected to accumulate even higher concentrations of this contaminant. This study conclusively shows that some vascular plant species are capable of extracting significant amounts of weathered SDDT from soils into their tis-

ues. In particular, Cucurbita pepo species are promising phytoremediators of SDDT. It has been estimated that the cost of phytoremediation as a clean-up strategy is far less than that of current conventional methods. For example, it has been determined that the cost of phytoremediating a one acre site is \$2000–\$4000 versus \$600,000–\$2.5 million for landfilling the same volume of soil (McIntyre & Lewis 1997). Hence, phytoremediation can be a cost-effective approach for cleaning up some pesticide-contaminated sites. Studies are currently underway to enhance the uptake of SDDT using soil amendments such as surfactants and organic acids.

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FULL SCALE CASE: SUCCESSFUL IN SITU BIOREMEDIATION OF A HCH CONTAMINATED INDUSTRIAL SITE IN CENTRAL EUROPE (THE NETHERLANDS)

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SUMMARY

TNO and Tauw have successfully carried out the first full-scale in situ HCH bioremediation at a contaminated site. This success was possible through a new approach that allows existing bacteria in the soil, groundwater and wastewater treatment plant to mineralise all HCH isomers into harmless end products like CO₂. Calculations for this industrial site in the Netherlands (Europe) have shown that the cleanup technology is 20-35% cheaper than the best alternative containment technology including Pump & Treat.

More important, the opportunity for combining waste management, remediation and redevelopment has already resulted in major investments by local investors. The result is a fully restored economic viability of the site while using bioremediation as a cleanup strategy. Injection of biological enhancing substrates created the desired groundwater conditions for the bacteria to degrade HCH. Overall monitoring results have proven complete mineralisation.

BEYOND STOCK/WASTE REMOVAL: CLEAN SOIL AND GROUNDWATER AND REDEVELOPMENT

The pollution of soil and groundwater with stocks and wastes are causing serious environmental problems. "Obsolete pesticides" like hexachlorocyclohexane (HCH, lindane) have gained large political attention over the last years. Central and Eastern Europe (CEE), the Newly Independent States (NIS) and Africa have put it on their agenda. On top of nationwide inventories, disposal programs and prevention policies the availability of faster, better and cheaper ex situ and in situ remediation technologies will become crucial.

Waste management of pesticides is a precondition for the establishment of a sustainable publicly accepted strategy. It contributes to the human and environmental viability of a contaminated site. The availability of a sound remediation solution for clean soil and groundwater is a necessity for responsible future use of the whole area. It will determine the economic viability of a contaminated site. In combination with options for redevelopment, investors are interest-

ed to participate and invest. An acceptable break-even point (investment versus profits) for all stakeholders will determine the chances of success. In some cases the investment costs for remediation may become part of the total redevelopment investments.

By looking beyond stock/waste removal, sites with negative values may be turned into sustainable and profit-making sites.

HISTORIC AND PRESENT SITUATION

The pollution of soil and groundwater with stocks and waste of hexachlorocyclohexane (HCH) are causing serious environmental problems. Lindane (gamma-HCH) is the best known and effective insecticide component of HCH. In the 1950s it was produced and stored at an industrial site in The Netherlands. Only 17% of HCH consists of the active gamma-isomer, lindane. The remaining part consists of alpha-, beta-, delta- and epsilon-HCH, which do not have insecticide activity. These isomers were separated from gamma-HCH and dumped as waste at different spots on the site. This area is redeveloped and bioremediation is taking place.

RISK ASSESSMENT OF THE SOIL AND GROUNDWATER CONTAMINATION

Although HCH waste has been removed in the past, it had already resulted in polluted soil and groundwater. Up to 1998 the soil and groundwater has been contaminated over a length of 200 meters, a depth of 18 meters and a width of 40 meters, with maximum concentrations of 2400 ug.l⁻¹ HCH. During the field characterisation in 1999 HCH-isomers and its degradation products monochlorobenzene and benzene were detected in the groundwater.

The conclusion of the risk assessment was that there is no risk for humans, because HCH is not present above the maximum concentration and that there is no ecological risk for the site because of its industrial application. Nevertheless, the contaminant distribution exceeds the volume criterion of 100 m³ per year and the contaminants flow towards the canal water (Figure 1). In Dutch legislation this means that there is an urgent situation and measures need to be taken.

REMEDICATION OPTIONS

In 1998 a consultancy firm made an overview of remediation options. Excavation was not feasible because of the high cost. The best solution in order to clean the site and to protect the canal against outflow of contaminants was a geohydrological interception using Pump & Treat technology. This is not an active remediation in terms of mass removal but containment for many years (> 50 years). The total remediation cost - excluding the cost for wastewater treatment - was estimated at 1.6 Million €.

At that time no in situ bioremediation alternatives for HCH were available. From literature it was known that one of the HCH-isomers, beta-HCH, was recalcitrant towards biodegradation under both anaerobic and aerobic conditions, posing a serious risk for the adjacent surface water. All other isomers are known biodegradable under both aerobic and anaerobic conditions.

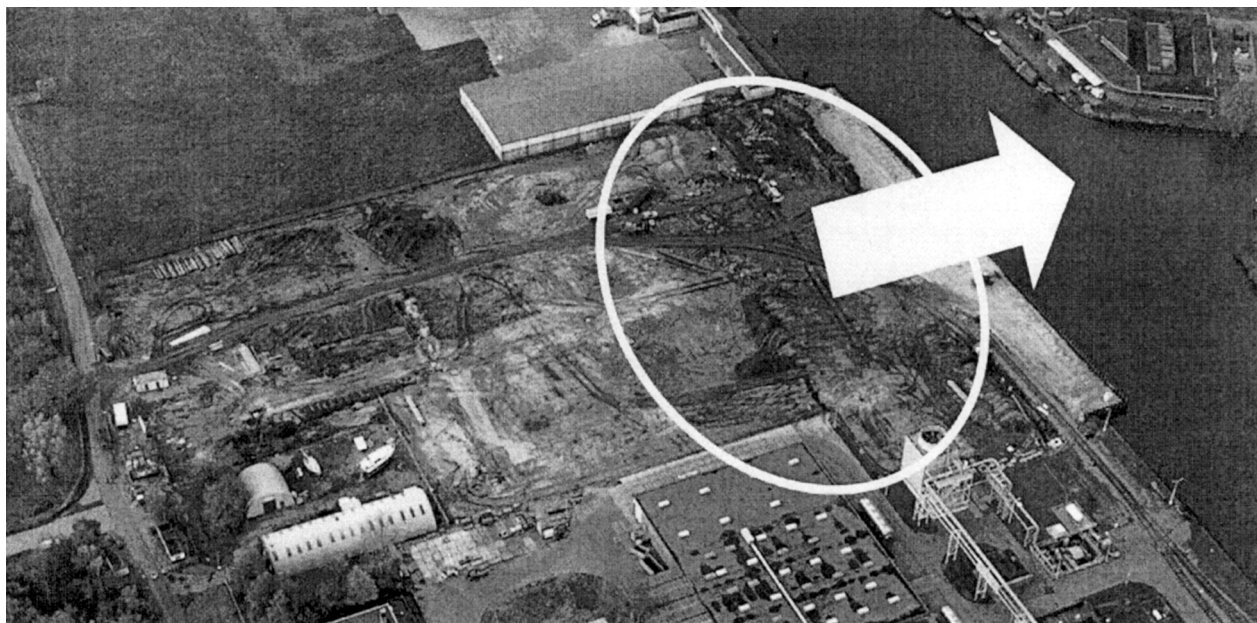


Figure 1: Flow of contaminants towards the canal water

A research project at the University of Wageningen proved that beta-HCH can be microbiologically degraded to the intermediates monochlorobenzene and benzene under anaerobic conditions using a natural substrate as electron donor. The intermediates can be biodegraded fast under aerobic conditions. Only for benzene it is known that very slow anaerobic degradation is possible. Up till now anaerobic degradation of monochlorobenzene has not been proven.

Thus, by applying the appropriate conditions – creating sequential anaerobic and aerobic zones - complete mineralisation of all HCH-isomers can be expected in the field (Figure 2).

In 1999 a Research & Development project was setup with the following objectives:

- Assessment of intrinsic (natural) biodegradation in the field and enhanced biodegradation in the laboratory with site specific material
- Full scale testing of an in situ bioremediation in the field by infiltration of substrate
- Assessment of cost benefits compared to Pump & Treat

LABORATORY TESTS: BATCH EXPERIMENTS

Anaerobic and aerobic batch experiments were performed with material from the site and successfully proved the complete degradation of HCH. The tested substrates ('electron donor') showed enhanced anaerobic biodegradation (Langenhoff et al., 2002). The gained information of the batch experiments was applied and used in the full scale test at the site.

DESIGN AND SETUP OF IN SITU BIOREMEDIATION COMBINED WITH SITE REDEVELOPMENT

Based upon the results of the geohydrology, the groundwater movement, the biodegradation velocity of HCH and

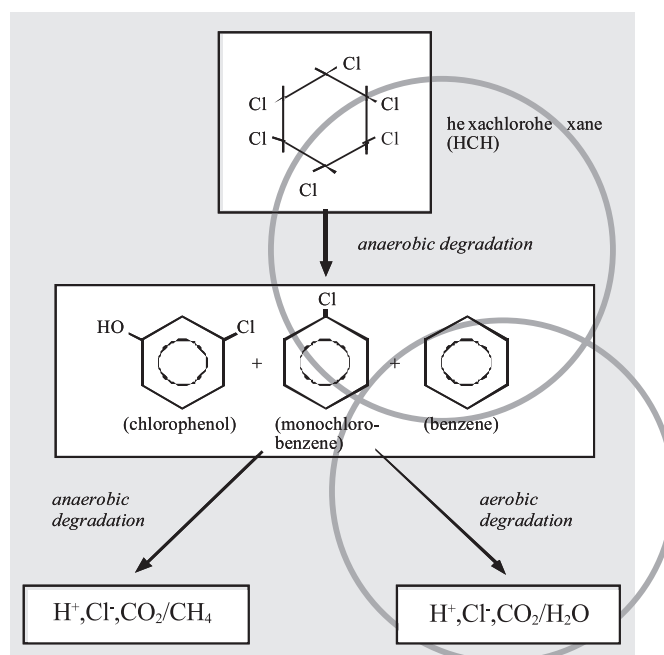


Figure 2: Biodegradation Pathways of HCH, monochlorobenzene and benzene under specific environmental conditions.

the groundwater characterisation, the design of the in situ bioremediation was made. Due to the redevelopment at the site the bioscreen consisted of an in situ anaerobic phase followed by an ex situ, aerobic phase.

At the same time of the design of the bioremediation system, local investors studied the feasibility of a container terminal to improve the cargo facilities of the local industry and to reduce transport by car. They realised that it was economically favourable to build the container terminal on top of the in situ remediation (Figure 3A, B). Both plans were integrated.

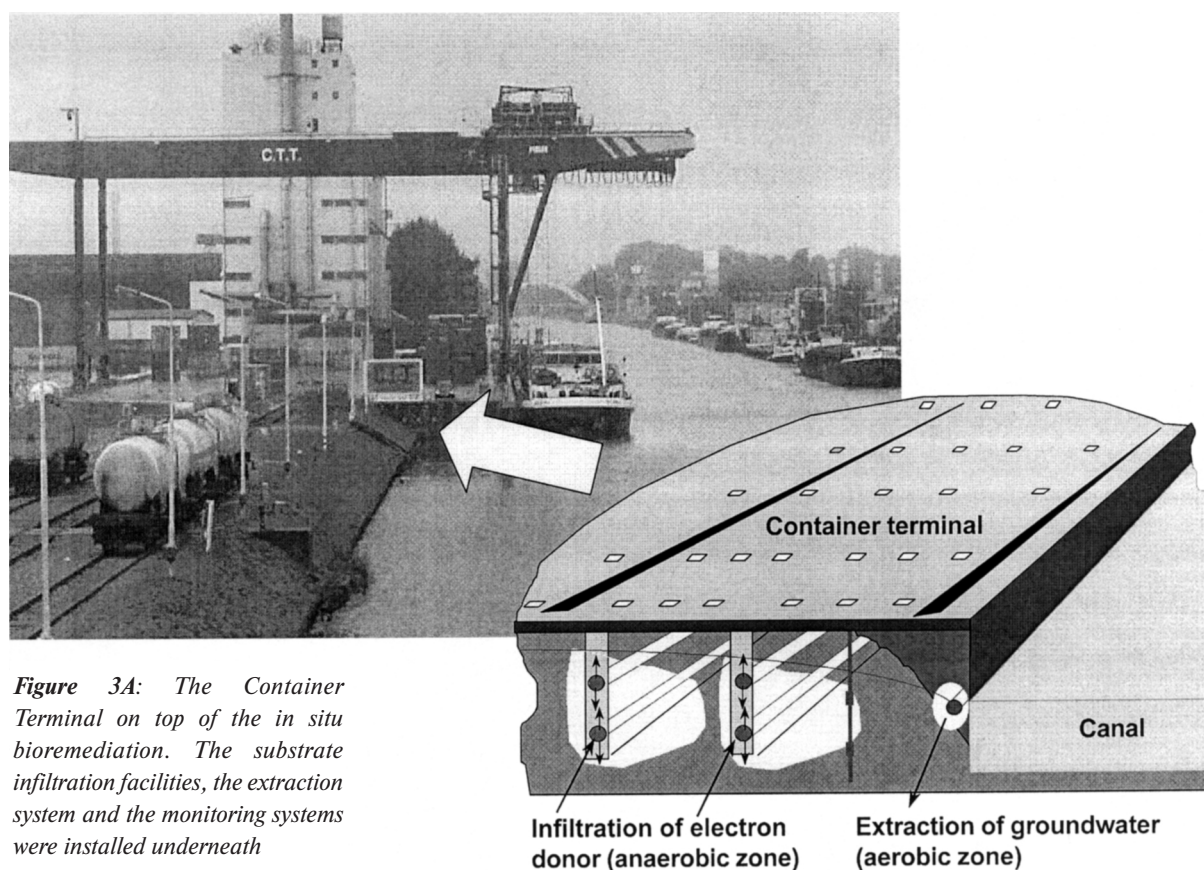


Figure 3A: The Container Terminal on top of the in situ bioremediation. The substrate infiltration facilities, the extraction system and the monitoring systems were installed underneath



Figure 3B: Top view of the site

With an investment of 4.2 Million € the container terminal was constructed at the border of the canal forming the boundary of the site. A new sheet pile wall was constructed in such a way that ships could easily stop there, the crane had easy access and heavy containers could be stored safely.

The substrate infiltration facilities and monitoring systems were installed under this container terminal. The anaerobic phase was designed as a bioscreen in which the HCH could be degraded into the intermediates monochlorobenzene and benzene. The drain was filled with electron donor. This substrate flew with the groundwater towards the extraction

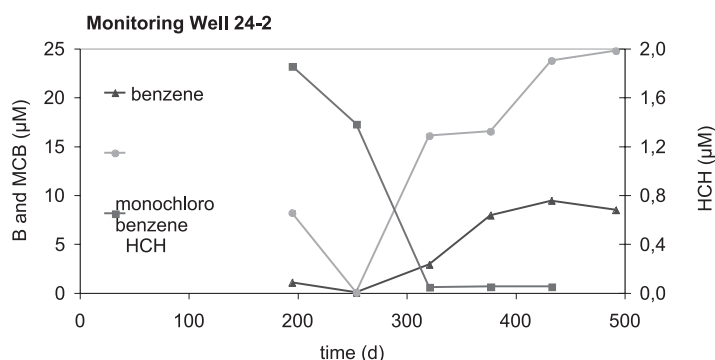


Figure 5: The concentration profile in monitoring well 24-2

drain, thus creating an anaerobic zone. The water from the extraction drain is pumped at a very low rate to the aerobic wastewater treatment plant. In the wastewater treatment plant the intermediates monochlorobenzene and benzene are aerobically degraded into the harmless end products carbon dioxide and water. The bioscreen has a length of 150 m and consists of two parallel drains at respectively 20 m and 40 m distance from the sheet pile wall. At the site, monitoring wells have been installed at various depths to follow the biodegradation processes.

The infiltration with electron donor has started in December 2001. The exploitation of the container terminal has started in August 2001. With an average of 45,000 container movements per year the break-even-point will be reached at the end of 2003.

FIELD RESULTS: INFILTRATION AND MONITORING

An initial monitoring programme, before infiltration had started, showed natural biodegradation of HCH. The breakdown products – monochlorobenzene and benzene – were detected in the core of the HCH-plume. The monochlorobenzene concentration remained constant in the first aquifer, whereas the concentration of benzene decreased, indicating complete biodegradation of part of the intermediates.

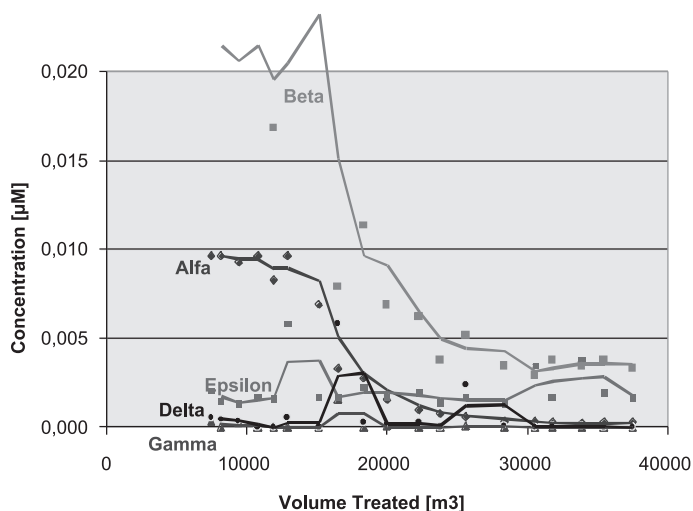


Figure 6: The concentration profile in the extraction drain

The infiltration system has been in use since 2001. The concentration of HCH has decreased quickly and the intermediates monochlorobenzene and benzene are increasing in time or are at a steady state value, indicating biological degradation in the infiltration area (Figure 5).

Benzene and monochlorobenzene are not produced in a stoichiometric ratio compared to the measured HCH concentration in the groundwater. This is due to their differences in retardation (adsorption-desorption) properties. Due to the slow desorption of HCH from the soil particles, free HCH in the groundwater, near to the injection well, is most probably biodegraded immediately. The concentration of HCH is near the detection limit.

The groundwater from the whole area is finally collected in the extraction drain and pumped to the aerobic wastewater treatment plant. A second proof of the positive effect of substrate dosing is the decreasing concentration of the various HCH-isomers, including beta-HCH, in the extraction drain. From the beginning of the pumping these samples have been analysed (Figure 6).

OVERVIEW OF COSTS

With positive results after 2 years of full scale testing a theoretical calculation of cost benefits compared to Pump & Treat was carried out. For this case - an anaerobic in situ bioremediation followed by an aerobic degradation in the local waste water treatment plant - the following phases were calculated and compared to the original geohydrological interception using Pump & Treat for many years:

- 1) Site investigation;
- 2) Design and Setup;
- 3) Infiltration (yearly);
- 4) Monitoring and Management (yearly).

The in situ bioremediation costs were calculated for 5, 10 and 15 years of infiltration. Herein the cost for the wastewater treatment was excluded due to the fact that they were never calculated for the original Pump & Treat approach and therefore could not be compared:

- 1.0 Million € with 5 years of infiltration;
- 1.2 Million € with 10 years of infiltration;
- 1.3 Million € with 15 years of infiltration.

Based on the results after 2 years, it is to be expected that the bioremediation may last 5 to 10 years. In this case the bioremediation system will give a cost reduction of 20-35 % compared to the Pump & Treat system.

CONCLUSIONS

TNO and Tauw have successfully carried out the first full-scale in situ HCH (pesticide) bioremediation at an industrial site and proved the possibilities of biodegradation.

Parallel to the bioremediation the construction and exploitation of a container terminal has proved its extra investment with a break-even-point already at the end of 2003. By looking beyond stock and waste removal, this site with its negative value (due to its contamination) has been turned into a sustainable and profit making site due the redevelopment investments (Figure 7).



Figure 7: Beyond Stock/Waste Removal: Clean Soil, Groundwater and Redevelopment

On top of nationwide inventories, disposal programs and prevention policies the availability of faster, better

and cheaper ex situ and in situ remediation technologies will become crucial for the establishment of a sustainable strategy and public acceptance in the world.

The perspectives for the application of in situ bioremediation to other pesticide and insecticide contaminated sites are numerous. Not only this in situ approach (combination anaerobic and aerobic treatment) has become a proven technology, it's also more cost-effective. Calculations for this industrial site in the Netherlands (Europe) have shown that the cleanup technology is 20-35% cheaper than the best alternative containment technology, including Pump & Treat.

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SUMMARY OF SESSION ON: PRECAUTIONARY PRINCIPLES FOR SUSTAINABLE USE OF PESTICIDES

Vicente Santiago and Tatyana Stefanovska

During the session the following points were highlighted:

- There is a need for continuous efforts to increase awareness and education in the pesticide users community so that potential health risks could be reduced. Companies producing pesticides should also engage in this effort so that proper storage, manipulation and disposal of the pesticides should be done in accordance with the specifications. It was also stressed by Mr. Frei (Syngenta Foundation) that it is very important to find the proper and efficient mechanism for communication with the farmer's community so that basic procedures to reduce health risks such as washing hands and change of cloths is done after spraying. A case study in Mexico supported by a Large Chemical Company serve as an example to prove health risks and attitude of farmers towards the use of pesticides despite efforts of awareness and education.
- There are numbers of approaches and techniques to control pests which include biological control. Various examples were presented from Asia, Africa, Latin America and Europe to show the good efficiency of this method. Still, Prof. Basedow highlighted the fact that in some cases there is a need to combine biological control with the application of pesticides. As a recommendation it was pointed out that in order to avoid potential environmental problems due to the introduction of alien species there is a need to follow the FAO directive.
- Mrs. Ms. Jones presented examples related the collection, disposal and recycling of obsolete pesticides and containers in the USA with particular focus in places like Illinois and the other Great Lakes regions. On the subject it was explained that various efforts like the "clean sweep campaign" were very interesting and successful whereby the government and farmers together with some associations managed to work together towards solving particular problems such as the disposal of obsolete pesticides and the containers which resulted in policy drafting and enforcement;
- Mr. Draga presentation was related to the use of plant growth regulators as potential mechanism to protect some plant species from pests particularly fungi with excellent results although it was highlighted that more research was needed under different conditions to corroborate the results.

At the end of the Session there was a lively discussion amongst the participants particularly in relation to policy similarities and differences between the European Union and the United States in terms of information related to handling and labeling pesticides and their containers. This discussion was of much interest to the experts from Ukraine as they highlighted that the country is following the USA policy but also they have to consider the EU position.

SAFE AND EFFECTIVE USE OF CROP PROTECTION PRODUCTS IN DEVELOPING COUNTRIES

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ABSTRACT

This paper summarises the work of a seven-year-long research programme that looked at the best way to reduce pesticide use among low-income farmers in developing countries while improving the effectiveness with which they used the products and the safety of their practices. The research was undertaken as part of a Risk Fund set up by Novartis in 1988 to support its business activities in the Third World; the study was sponsored by the Novartis Foundation for Sustainable Development.

The project draws attention to the fact that if farmers were to take a series of relatively simple steps, they could reduce their exposure to pesticide-related health risks. At present, many if not most farmers give low priority to “safety”, and many have not adopted the necessary precautions to reduce health risks. Some procedures may well be made more acceptable to low-income farmers—for example, by developing and subsidising the sale of both cheap and comfortable clothing that can provide adequate dermal protection. In the main, though, it appears that there are few if any easy ways to promote change among large numbers of poor smallholders.

There will have to be a continued reliance on sustained efforts such as some of those incorporated in this project. Any pesticide manufacturer that cannot guarantee the safe handling and use of its high toxicity products should withdraw those products from the market. At the same time, since in all likelihood pesticides will continue to be the technology of choice for crop protection in the years ahead, there is a continued need to get farmers to adopt the most important risk-reducing procedures.

BACKGROUND

The ability of the world's farmers to produce food has improved dramatically over the past four decades. Yields of maize, rice and wheat nearly doubled between 1960 and 1994 and similar progress was made in other crops. Achievements such as these were due largely to technological progress in the form of improved varieties, irrigation, fertilisers, use of crop protection agents and a range of technologies that aided farmer's management of crops and resources. This increased output can be demonstrated by using the output achieved in India over 20 years. From an average yield of 0.95 tonnes per hectare of grain in 1961-63 the yield had increased to 1.98 tonnes of grain per hectare in 1991-93. The key components for this Green Revolution were the use of modern seed varieties, fertilisers,

irrigation, mechanisation and insect and weed control. Benefits were seen both by the rich and the poorer landowners. In addition the increased food production has led to general decreased food costs and improved food security.

The use of crop protection products in rural areas of the developing countries beset by poverty has been a highly controversial topic for many years. Criticism of the use of pesticides in the developing world was summarised by Conway (1997) saying that “Pesticides not only cause or aggravate pest problems, they contaminate the environment and may have serious consequences for human health”. However there are proponents of the use of pesticides who estimate pest-induced production losses. From analysis Oerke et al. (1994) found that pathogens, animal pests and weeds can cut the potential production of nearly all food crops by half.

The opponents of chemical crop protection raise the following main criticisms against the products and their manufacturers:

a) Due to the prevailing conditions in developing countries (illiteracy, ignorance of side effects etc.), the safe and proper use of chemical crop protection agents cannot be guaranteed. This can lead to the possibility of pesticide residues in the harvested produce.

b) The inappropriate use of these products can be downright counterproductive, above all for small-holder farmers: the costs to the environment and health outweigh the benefits. The indiscriminate use of pesticides harms useful organisms more than it does the pests, and thus exacerbates the pest plague while making the farmer dependent on chemical weapons.

c) In the face of stagnation of pesticides in developed countries, the pesticide industry is expanding in developing countries with more and more aggressive marketing methods while cutting back on applications guidance.

As result of these criticisms, broad sectors of the public hold a general sceptical or even adversarial attitude toward chemical crop protection and the manufacturers. Pressure groups in particular have placed their stamp on media coverage and on the information databases of parliamentary investigating committees and on social science institutions.

There are many issues which make it difficult to form a sound judgement on the benefits or otherwise on the use of pesticides. There are around 800 active ingredients of pesticides, each with different characteristics and spectrum of activities. Some are over 50 years old, are now considered too dangerous and non-selective and are used at rates of kilos per hectare. Most have been banned by regulatory authorities in industrial countries yet are produced and sold at very low prices in many developing countries. Most modern products on the other hand are highly selective with low toxicity to humans and other non-target organisms. They are often applied in quantities of a few grams per hectare but are mostly considerably more expensive than older products.

Although many experts are convinced that important aspects of chemical crop protection can be scientifically

demonstrated, data are lacking on whether the safety problems associated with their use are in fact due to lack of knowledge, "bad" habits (despite knowing better), or lack of access to protective devices. Health statistics have been used to attempt to understand the effects of pesticides on humans. However most statistics do not differentiate between occupational health problems and the intentional misuse for suicide and murder. There is strong evidence of widespread use of pesticides for such crimes. For example in a report of 400 cases of poisoning from pesticides in a five year period, the great majority were found to be attempted suicides using organophosphates and none of the incidents were connected with the person's occupation.

RATIONALE FOR THE PROJECT

In today's public debate and discussion, responsibility for damaging human health and the environment, as well as for the resulting economic losses through the use of crop protection products, is almost exclusively attributed and shifted to the manufacturers. As a consequence, critics urge either to reduce drastically or even to prohibit distribution and sale of crop protection products to small-holder farmers in developing countries.

Against this background a manufacturer basically only has the following alternatives:

- a) Carry on trading as normally, closing his eyes to the critics with the consequence that in the long term a hostile social environment may develop as well as an increasing regulatory framework which will reduce the market potential or.
- b) A commitment which goes beyond conventional marketing, sales and information practices and which is well understood and used by the manufacturer to secure long-term business success.

The assessment of the risks versus the benefits of pesticides use is complex and difficult to quantify. Crop protection products undoubtedly contribute to the increased production of affordable foods in developing countries. However the evaluation of the damage they cause to humans, natural enemies and the environment is necessary and demands the rational collection of facts and figures. Therefore in January 1991 the former CIBA-GEIGY Foundation approved a Risk-Fund Project in order to bring forward an innovative approach along the lines of the second alternative mentioned above, with the following objectives:

- a) To produce evidence that a crop protection products manufacturer can have constructive interest in the perception of the problems of small-holder farmers in developing countries without any ideological hidden agenda and on scientifically sound and workable solutions for those problems. It goes without saying that the participation of external consultants and critics are part of an element for enhancing credibility.
- b) To shape constructive dialogue and contribute to the debate on safety and effectiveness of crop protection products through a self-imposed empirical research study.

OBJECTIVES

The Risk Fund Project was launched to answer the following questions:

- a) What factors hinder the safe and effective use of crop protection products in developing countries?
- b) What sort of groundwork must or can the manufacturer, in collaboration with other institutions and organisations (agricultural extension services, for example), undertake to eliminate these factors?
- c) In a given socio-cultural context, what communication methods are best suited to furthering rational and safe use of crop protection products?

RESEARCH GOALS

To obtain a broad database covering various socio-cultural and economic factors that shape Knowledge, Attitudes and Practices, a so-called KAP-Study was mounted with questionnaires established containing ten key messages on safety and seven on effectiveness. These questionnaires served as parameters in the surveys carried out during the project and having been tracked throughout the different phases. Its main objectives were:

- a) To acquire insight into knowledge, attitudes, and practices of the target groups as these relate to crop protection and the use of crop protection products;
- b) To gauge the significance of knowledge and attitudes for the rational and effective use of crop protection agents;
- c) To establish indicators that can be used to measure future changes in KAP; and
- d) To analyse differences and similarities in the three geographically and socio-culturally dissimilar study sites, with a view to determining whether standardised modes of intervention for increasing the safe and effective use of crop protection products are possible.

HYPOTHESES OF THE PROJECT

Hypotheses were established that through communication and training, specific aspects of safety and effectiveness could improve farming practice. These were measured and tracked throughout the project.

- 1: Reduction in dermal contamination leads to reduction of possible health problems.
- 2: Proper handling and use limits negative impacts on the environment.
- 3: Effective handling and use improves economic situation of farmers.
- 4: Farmers value economics more than safety.

DESIGN OF THE PROJECT AND ORGANISATION

In order to collect as broad an experience as possible the study was carried out in three developing countries with totally different socio-cultural environments and structures, although with similar economic and technological standards. The countries were India, Mexico and Zimbabwe.

In each country an "intervention region" was selected as the site of an information, education and communication program. For comparative purposes in all three counties, a control region, or a no-intervention zone, was also desig-

nated and where possible located far enough away to preclude any influence from the above program.

The project areas in the three countries were as follows:

The Coimbatore district in India was chosen. The intervention programme was tested in the Udumalpet block. The control area was defined as the rest of the district.

In Mexico the communication campaign was undertaken in the southern state of Chiapas bordering on Guatemala. The Villaflores region was chosen as test, and the Cintalapa region as the control area.

In Zimbabwe the project was carried out in the communal lands of Sanyati in the Kadoma district.

Heading the project was an international Steering Committee consisting of staff from Basel Crop Protection Division, the Novartis Foundation for Sustainable Development, and representatives of the Agricultural divisions of the three participating Novartis Group Companies, together with independent outside experts and a critical freelance journalist. The Indian Market Research Bureau (IMRB) was responsible for the studies and their evaluation.

The target farmer groups chosen were small-scale cotton growers in India and Zimbabwe and maize growers in Mexico. Four distinct project phases were established: Phase one, from 1991-1993, production and evaluation of the baseline KAP; Phase two, from 1994-1997, tailor-made interventions such as the use of film, video and pest scouting booklets in India; radio programs, children's drawing booklets and cartoon-stories in Mexico; folk theatre plays, demos and insect pest calculators in Zimbabwe, just to mention a few of the selected items, and evaluation of end-line KAP; Phase three, from 1997-1998, cessation of any intervention and follow-up of persistence of impact; phase four, from 1998-1999, with evaluation of results, calculation of net change with interpretation, conclusion and writing-up for publication. The results of the study were presented to FAO at Rome end of 1999.

SUMMARY OF RESULTS

Baseline KAP

Related to knowledge of safety aspects, farmers know little about health risks and hardly any measures and precautions to reduce them.

Related to safety attitudes farmers do not admit health risks and/or perceive them as inevitable.

Safety and effective pest control are perceived as contradictory concepts. Examples supporting that are as follows: In India farmers perceive health risks as occupational hazards (fatalistic attitude). In Mexico farmers do not admit physical vulnerability (machoism). In Zimbabwe farmers state that in their fight for survival they expect to suffer at least some wounds.

Related to practices pesticide users make few efforts to prevent health risks, with the exception of those who have suffered intoxication symptoms, they try to reduce by improving their safety gear and avoiding spraying personally by hiring spray operatives (as is the case in India).

Knowledge, although low, exceeds practices, but it does not really translate into practicable action. With regard to knowledge on effectiveness of pesticides it varies greatly between countries and farmers.

The attitudes confirm that pesticides are perceived as a necessity. In practices great variations and experience levels are observed.

Endline KAP

The results of the endline KAP evaluation were compared to the baseline analyses conducted at the start. A further follow-up survey was done a year later in order to assess long-term impact.

Results were then categorised into two groups according to their persistence or continuation of adoption, viz. continued vs. discontinued changes of desired traits.

Relating back to the hypotheses established at the start of the project, some specific changes in farmers' attitudes and practices which have been tracked are as follows:

Hypothesis 1

Trough communication and training we will improve practice in:

- skin protection,
- preparation of spray solution,
- washing of body and work clothes,
- spraying and application, and
- maintenance of spraying equipment.

In Mexico personal safety has been improved persistently by using shirts, boots and footwear; in the washing of work clothes and hands in sprayer cleaning and in utilising measuring devices. The project had a favourable impact on comparatively simple, cheap safety practices, while more cumbersome practices did not change for long or were even used less.

In India the practice of having a full body wash after spraying rose significantly and was sustained. Use of gloves for mixing pesticides however showed small improvement but dropped after intervention. Significant improvements were registered in maintenance of sprayers. Precautions taken before breaking for food and drinking persisted. Use of protective clothes dropped.

In Zimbabwe personal hygiene measures were already at a high level when the project started, but the project had a further positive impact. Another significant increase was reported in the regular washing of work clothes. Overall the project had a positive impact on reported attitudes regarding personal hygiene and skin protection.

Hypothesis 2

Through communication and training we will improve practice in:

- optimisation of pesticide used and of spray parameters,
- storage of crop protection products, and
- disposal of empty containers.

This area showed favourable changes in Mexico. Persisting changes included storage of pesticides and

avoiding repacking, and disposal of empty containers were improved.

In India the safe disposal showed no improvement in either area. The program ensured that good practices more or less continued.

The correct disposal of empty pesticide containers improved in Zimbabwe. The introduction of the cotton pest calculator aiming at improving the use of the optimum quantity of pesticides showed an invisible result, this tool would require a more comprehensive introduction and training.

Hypothesis 3

Through communication and training we will improve practice in:

- identification of pests and beneficial insects,
- selection of suitable product,
- determination of correct dosage,
- usage of suitable equipment,
- correct timing of application, and
- correct application techniques.

In Mexico knowledge of beneficial insects improved and in focus group discussions more rational attitudes towards pesticides were detected. In India, inspection of plants before a spray decision is taken improved significantly as did the choice of the pesticide to be used, but this change did not continue. The same applies to the knowledge on beneficials, as did the spraying techniques. In Zimbabwe knowledge of beneficials remained at a moderate level.

Hypothesis 4

Improvement of farmers' economics will facilitate their adoption of messages on safety. In Mexico it seemed as if demonstrations of more productive crop protection techniques made by the project staff raised the farmers' level of interest and thus increased the level of trust, which in turn facilitated communication. More rational attitudes towards pesticides affected farmers' perception of both effectiveness and safety issues.

In India there was widespread appreciation among farmers that Novartis had put considerable effort into the improvement of their health by teaching them how to enhance their safety as well as improve crop yields through the effective use of pesticides.

In Zimbabwe's drought in 1995/96, which meant the loss of food as well as cash, crops had a very negative impact on the farmers' economic situation. This external pressure manifested clearly that under such conditions the farmer gives priority to spending his funds first for basic needs before investing in safer pesticide use.

Overall, the interventions did have a positive impact. A fundamental lesson learned was that messages must be practical, basic and ready-to-use. Suggesting the use of impractical or expensive items or habits can dilute the overall message about safety precautions. A highly technical and expensive approach is not needed to improve safety.

RECOMMENDATIONS

In the following recommendations to manufacturers and other stakeholders of crop protection are brought forward:

- On-going multi-stakeholder approach is needed. Single manufacturers with isolated endeavours only can have a very limited effect. In order to achieve a real difference, actions from all stakeholders and concerted efforts of regulatory authorities, extension units with the ministry of agriculture, trade channels, NGO's, farmers' organisations etc. together with pesticide industry and its associations have to be pooled together.

- Research-based companies vs. generics oriented industry. In this connection we ought to address and reconcile the differing views between the two conflicting sides. This point needs serious discussions between industries, regulatory bodies and industry associations. All efforts shall be taken to get all parties on board, make them participate and join the multi-stakeholder group's endeavours.

- Incorporate social into commercial marketing. Social marketing was described by Kotler and Zaltman (1971) as the use of marketing principles and techniques to advance a social cause. It is suitable to achieve required changes in attitude, but it needs to be done on a sustained basis, as farmers tend to fall back into undesirable attitudes and habits. It has to be part and parcel of commercial marketing.

- Product and portfolio changes may also be envisaged if safe use of products of toxicity class 1A+1B cannot be guaranteed. Industry should not create a technological apartheid system by depriving small farmers of developing countries from latest innovations and technologies. Manufacturers should be innovative in branding, packaging and pricing.

- Developing countries should give highest priority to an agricultural policy which provides motivation, security and stability to risk-averse small-holder farmers. However external support is needed to assist these governments.

- Product stewardship efforts are not sufficient. Stewardship efforts have to be much intensified and be more directed to the needs of resource-poor farmers. In many instances manufacturers as well as trade channels do not play a sufficient determined and active role in training and communication. They hardly have any presence which is directed to that farmers' segment. Some companies have had commendable activities in the past, but given them up due to economic constraints. This situation needs a re-orientation and to be drastically improved if industry wants to be credible.

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OBSERVATIONS AND EXPERIMENTS ON THE POSSIBILITIES OF REDUCING THE USE OF SYNTHETIC PESTICIDES

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ABSTRACT

Based on own world-wide research in Germany, the Philippines, Panama, the Sudan, and Egypt, the possibilities of reducing the use of synthetic insecticides are shown, together with the limitations given.

INTRODUCTION

In seven areas of the world, six factors were observed, which led to the reduction of insecticide use. 1. Reduction of subsidies to farmers (by EU): Effects studied in Northern Germany (Cereals & oil seed rape). 2. Education of farmers: Effects studied in Panama (Highland) (potatoes & carrots). 3. Use of Neem Preparations (Azadirachtin, Botanical): Effects studied in central Germany (potatoes, Fabaceae), and in the Sudan (potatoes, aubergine, okra & to-mato). 4. Use of *Bacillus thuringiensis*: Effects studied in central Germany (*B.t. morrisoni*: potatoes) and in Luzon, Philippines (*B.t. kurstaki*: cabbage). 5. Pheromone mating disruption, Lepidoptera: Effects studied in Egypt (cotton, Pink Boll Worm). 6. Introduction of natural enemies (from the original site of the pest): Effects studied in Luzon, Philippines (cabbage, Diamond Back Moth) (and in Papua New Guinea, mango, *Ceroastes rubens*; still under study). But, of course, there are also observations, when 3. and 5. did not work, to say it initially: 7. Necessity of use of synthetic insecticides (when economic threshold is reached). Observed in: a) Virus vectors in tomatoes (Panama, lowland, white flies on tomatoes), b) Onion thrips (Sudan), and

3) Spiny boll worm in cotton (Egypt). Nevertheless it should be pointed out that synthetic insecticides to some extent do not have the desired effect: 8. Failure of synthetic insecticides. Observed in Cotton in Pink Boll Worm in Egypt etc. Under these precautions, the six points will be regarded in detail below.

RESULTS

1. Reduction of subsidies to farmers (by EU)

Within the EU, in 1993 a large change of subsidising practice occurred. Suddenly, the farmers received considerably less money by the EU (Table 1). This fact led in Germany to a considerable decrease of use of nitrogen fertilisers and of insecticides in agriculture (Figure 1 and 2; BASEDOW 2002).

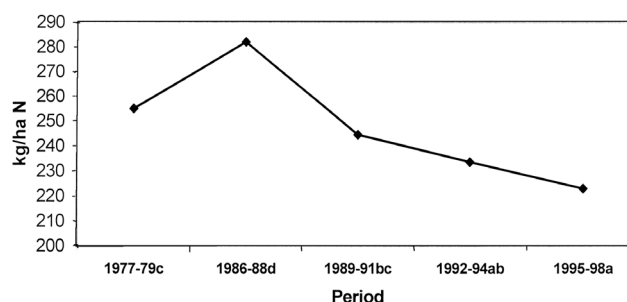


Figure 1: The changes of fertiliser use in an area in Northern Germany, 1977-98. Periods followed by different letters are significantly different ($p = 0.05$, Duncan)

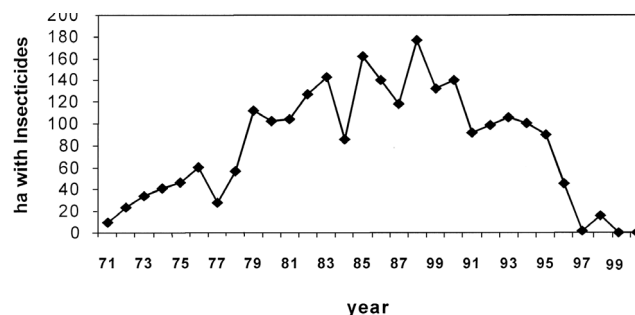


Figure 2: The acreage with insecticides in an area in Northern Germany (142 ha), 1971-2000.

Crop	Winter oilseed rape		Winter wheat	
Year	1985	2001	1985	2001
Price of Intervention, EU (DM/dt)	90,--	37,--	45,--	23,--
Maximum market price, after own storage (DM/dt)	104,--	40,--	59,--	27,--
Yield (dt/ha)	35	35	83	83
Maximum monetary yield (DM/ha)	3640,--	1400,--	4897,--	2241,--
Bonus per area (by EU) (DM/ha)	0	864,--	0	690,--
rBrutto**	3640,--	2264,--	4897,--	2931,--
Loss for farmer (DM/ha), 1985-2001	-1376,--		-1966,--	

* the variable costs still have to be subtracted

Table 1: Northern Germany, changes of subsidies by EU between 1985 and 2001 (crucial year: 1993). (2 DM – ca. 1 Euro – ca. 1 \$)

2. EDUCATION OF FARMERS

Educating farmers, to enable them to decide for a reduction of insecticide use: An example from the highlands of Panama (SONDER et al. 1997) (Table 2). Ing. agr. V. Rios, an educated farmer, used less insecticides and fungicides in potatoes, but more insecticides in carrots than his colleagues: he was apparently more aware of what he did than the other farmers.

Crop	Farmers	Herbicides	Nematicides	Insecticides	Fungicides
Potatoes	All Farmers (5)	1	1	19	19
	Ing. agr. V. Rios	1	1	6	9
Carrots	All Farmers (5)	1	0	3	14
	Ing. agr. V. Rios	3	0	5	10

Table 2: The number of pesticide applications by farmers, June to November, 1994, at Cerro Punta (ChiriquT, Panam3)

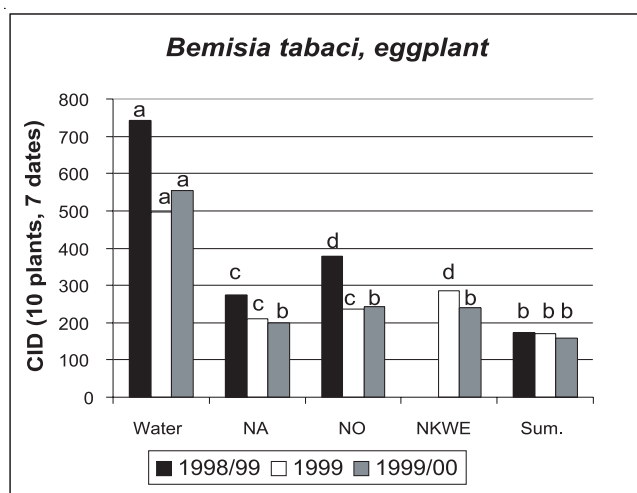


Figure 3: Cumulative insect days (CID) of *B. tabaci* on eggplant with different weekly treat-ments by ULV-technique, Khartoum-North, Sudan, 1998-2000.

3. USE OF NEEM PREPARATIONS (AZADIRACTIN, BOTANICAL)

Effects studied in central Germany (potatoes, Fabaceae) (BASEDOW et al. 2002), and in the Sudan (potatoes, aubergine, okra & tomato; EL SHAFIE & BASEDOW 2003; Mudathir & Basedow 2003). Some examples from the Sudan shall be shown.

Neem preparations, especially commercial NeemAzal®, proved to be as effective as Sumicidin, in controlling homopterous pests (Figure 3 & 4). Also the yield of aubergines and potatoes was increased in comparison with "Untreated" like in Sumicidin (Figure 5 & 6).

Columns of one year with different letters are significantly different ($p < 0.05$, Turkey)

4. USE OF BACILLUS THURINGIENSIS

A. Effects were studied in central Germany of *B.t. morrisoni* ("Novodor") on the Colorado potato beetle in potatoes (Table 3; BASEDOW et al. 1997). Only with two treatments per season, *B.t. morrisoni* gave significant

yield increase. NeemAzal proved to be more effective (for ineffec-tivity of neem, see below: onion thrips and virus vectors). B. In Luzon, Philippines, *B.t. kurstaki* was used successfully in cabbage (AMEND & BASEDOW 1997). Against Noctuidae, *B.t. aizawai* ("Xentari") is recommended.

Columns of one year with different letters are significantly different ($p < 0.05$, Turkey)

5. PHEROMONE MATING DISRUPTION, LEPIDOPTERA

Effects studied in Egypt, in cotton, with Pink Boll Worm (*Pectinophora gossypiella*) (BOGUSLAWSKI & BASEDOW 2001). In comparison with synthetic insecticides, mating disruption was perfect: it decreased the pest attack and increased significantly the yield (Table 4 and Figure 7).

6. INTRODUCTION OF NATURAL ENEMIES (FROM THE ORIGINAL SITE OF THE PEST)

Effects were studied in the Cordillera Region of Luzon, Philippines (cabbage, diamond back moth). Biological control of the diamond back moth *Plutella xylostella* on cabbage at Luzon, Philippines by introduction and establishment of its hymenopteran parasitoid *Diadegma semiclausum*, 1991-93 (AMEND & BASEDOW 1996). A summarising view on the effects and factors associated with the biocontrol is given in Table 5.

Columns in one season with different letters are significantly different ($p < 0.05$, Turkey).

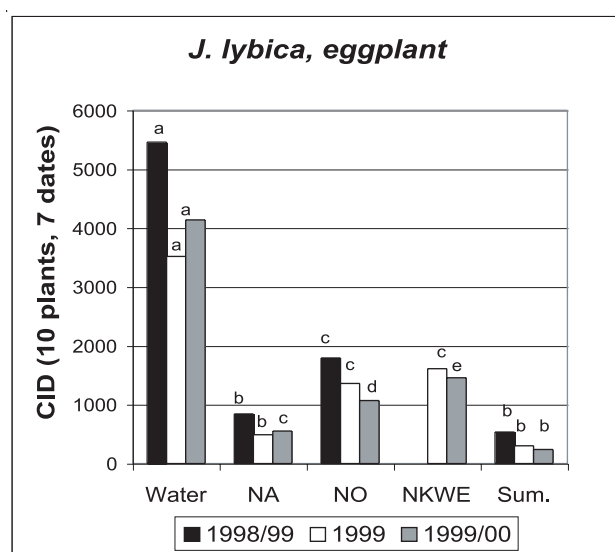


Figure 4: Cumulative insect-days (CID) of *Jacobiasca lybica* on eggplant with different weekly treatments by ULV-technique, Khartoum-North, Sudan, 1998-2000.

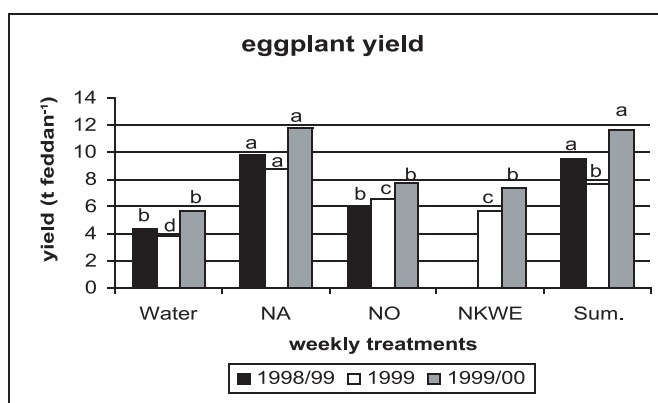


Figure 5: Effects of weekly treatments (with ULV technique) of different preparations on eggplant yield in three subsequent seasons at Khartoum North, Sudan.

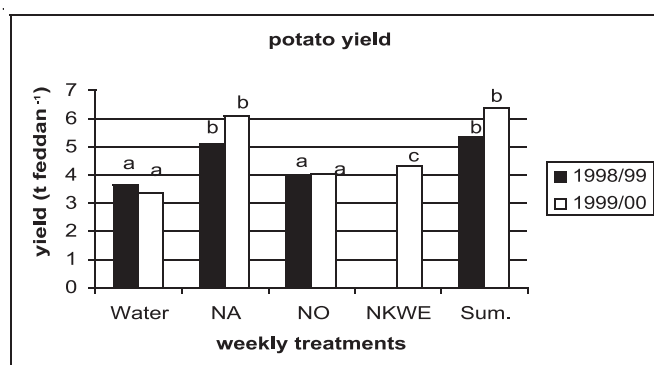


Figure 6: The yield of potato in two field experiments with different weekly treatments (with ULV-technique) at Khartoum North.

Year	No of treatments	Effects	Untreated	Novodor, 3l/ha	NeemAzal 0.5%
1995	Two	Damage (%)	73	19	7
		Yield (%)	100	119**	129***
1996	One	Damage (%)	72	58	54
		Yield (%)	100	109	123*

Table 3: Results of two field studies with control of Colorado potato beetle (*Leptinotarsa decemlineata*) near Frankfurt/M., Germany

Date 1999	Organic Cotton with mating disruption	Conventional Cotton with Insecticides ¹	Conventional Cotton without Insecticide
30.06.	0	14**	./.
11.07.	6	8	./.
20.07.	6	10	12
27.07.	6	10	10
04.08.	4	28**	./.
09.08.	8	34**	./.

Table 4: Boll-Sampling for *Pectinophora gossypiella* Infestations of Cotton in the neighbour-ring villages Sakaran and Talat (Fayoum), 1999. Pink boll-worms per 100 bolls per field and week.

¹ Esfenvalerate and Curacron – ** significant differences to Organic Cotton at $p = 0.01$

Positive effects	Supporting factors	Gaps of efficiency
Control of <i>Plutella xylostella</i>	Remains of cabbage harvest in the fields	<i>Spodoptera litura</i> (Lep., Noctuidae)
Reduction of strong insecticide use	Weed <i>Galinsoga parviflora</i>	<i>Pieris canidia</i> (Lep., Pieridae)
Recovering of the beneficial fauna (stabilising of the ecosystems)	Wild ornamental plant <i>Zantedeschia albomaculata</i>	<i>Lipaphis erysimi</i> & <i>Brevicoryne brassicae</i> (Hom., Aphididae)

Table 5: Observations around the successful release of *Diadegma semiclausum* in the Cordillera Region of Luzon, Philippines

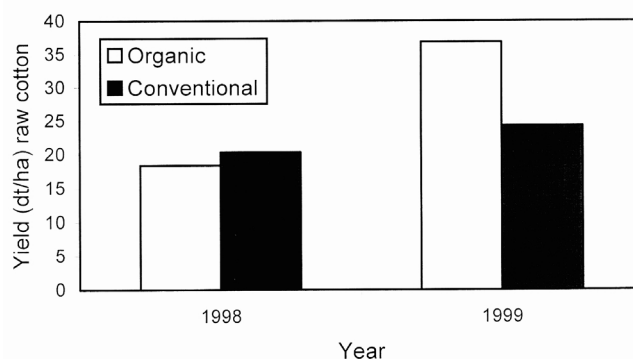


Figure 7: Yield of cotton, 1998 and 1999 in conventional and organic cotton. 1999: Organic cotton with mating disruption, conventional cotton with insecticides.

Columns in one season with different letters are significantly different ($p < 0.05$, Turkey).

Finally, after a lot of positive results, findings from tomato in the lowland of Panamá (peninsula Azuero) are to be shown, where viruses were inflicted (Table 6) (BASEDOW et al. 2002).

CONCLUSIONS

Concluding, it can be said that a lot of possibilities exist to reduce the use of synthetic insecticides. But the alternative methods are not always sufficient. So in IPM, both methods should be combined, but in this case only “modern”, environmentally and toxicologically harm-less ingredients should be used.

Treatment	Untreated (water)	NeemAzal T/S (10 mg AzaA/g),	Endosulfan (Thiodan, 350 g a.i./l)	Imidacloprid (Confidor 70 WG, 700 g a.i./l)
Dosage	600 l/ha	3 l/ha in 600 l of water (=30 g AzaA per ha)	1.5 l/ha in 600 l of water	1.: 500 g/ha; 2. to 4.: 250 g/ha in 600
Rhythm	Weekly	Weekly	Weekly	Three-weekly
No. treatments	11	11	11	4
B. tabaci on 10 leaves (average of 9 counts)	8.0±3.6c	6.2±2.7b	6.4±2.7b	1.1±0.9a
% reduction	0	-22.5	-20.0	-86.2
Virus symptoms (%)				
– before flower	77.3±11.8b	63.8±20.5b	61.4±3.4b	28.6±6.2a
– after flowering	18.0±8.5a	22.7±8.7a	28.4±9.5a	33.2±21.4a
Healthy plants (%)	4.7±4.3 a	13.5±14.0 ab	10.2±10.5 ab	38.2±25.0 b
Yield (kg/ha)	4022±1463ab	2679±631 b	4804±945 ab	6144±1304 a
% alteration	0	-33.7	+18.9	+52.0

Table 6: The effects of different treatments in tomato plots on *Bemisia tabaci*, virus attack and yield in Panama. Figures followed by the same letter are not significantly different at $p = 0.05$ (Turkey-test).

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NEW PHYSIOLOGICALLY ACTIVE SUBSTANCES OF NATURAL ORIGIN AS COMPONENTS OF SUSTAINABLE AGRICULTURE

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INTRODUCTION

Plant growth regulators (GR) play an important role in enhancement of productivity of cereals. Application of such regulators permits to regulate the most important processes in plants. An important result of application of the growth regulators is the increase of plants resistance to unfavorable environmental conditions, such as too low or high temperatures, drought, phytotoxic action of pesticides, plague of infections and pests.

The Institute of Bioorganic Chemistry and Petroleum chemistry of the Ukrainian National Academy of Sciences has conducted the complex research of new plant growth regulators for the last 10 years. In-depth research of physical and chemical properties of growth regulators based on N-oxides of pyridine derivatives has proved that these regulators have a number of unique qualities, which explain their high ability to regulate growth processes. Such regulators include Ivin (N-oxide 2,6-dimethylpyridine), Triman (aqua-N-oxide 2-dimethylpyridine Mn), and their derivatives [1]. These regulators are highly sensitive to slow mechanic vibrations, variations of electric and magnetic fields, and infra sound. Some of these mentioned properties of electronic or ion semiconductors allow them to transmit electronic and magnetic impulses and other signals. Study of test plants showed that Ivin has cytokinin and auxin activity.

We used Triman (a synthesized substance, derived from N-oxides of pyridine), Emistim and Agrostimulin in this study. Emistim is a product of metabolism of the roots' epiphytes such as *Panax ginseng* and *Hippophao rhamnoides*. It contains some amino acids, growth regulators and lipids. Emistim is a GR of natural origin. Agrostimulin is a mix of Ivin (a synthesized substance) and Emistim (a natural one). However the ratio of Ivin to Emistim is very small, which ensures ecological safety of this GR. The aim of our work was to study the physiological effect of Agrostimulin, Emistim and Triman on some stages of nitrogen metabolism and productivity of winter wheat in the conditions of Kyiv region; and to study the combined use of these growth regulators and fungicides during the pre-seedtime treatment of the winter wheat seeds.

METHODS

Plants: For our tests we used plants of winter wheat (*Triticum aestivum* L.) of 'Polisjka 90' sort. The experiments were carried out on our test plots (managed by the

Institute of Agriculture of the Ukrainian Academy of Agricultural Sciences, Chabany) in 1997-2002.

Experiment –Effect of the growth regulators in field conditions: Each test plot had an area of 10 m² with the light gray clay soil. The norm for sowing was 5 million grains per hectare. Each plot was fertilized with ammonium saltpeter (N120P90K90). The growth regulators were introduced as solutions by spraying onto the plots in the following concentrations: Agrostimulin – 5 ml/ha, Emistim – 5 ml/ha and Triman 50 ml/ha at IV-V stage of organogenesis. Nitrate reducing in wheat leaves was determined in vivo by the method of Mulder. We used the Kyedal's method for determination of the total content of nitrogen. However, we used spectrophotometric with the use of Nesler reagent instead of distillation. The quantity of nitrates in the plant leaves was determined using the potentiometer method. The grain quality was evaluated with an "Infrapid" device (USA), which allows us to measure the protein content in grain precisely.

Statistical Analysis: Data were analyzed using repeated measures analysis of variance. The statistical processing of our data was carried out using the dispersion analysis. All evaluations were made using an alpha level of 0.05.

RESULTS AND DISCUSSION

In the first part of our work we studied the physiological influence of these growth regulators on the nitrate-reducing ability of leaves, as well as the nitrates content, the total nitrogen content and grain productivity and quality.

The dynamics analysis of the total nitrogen accumulation in the flag leaf during the vegetation of 1997, for example, (Figure 1) shows that the regulators promote the nitrogen content increase. Action of Emistim and Triman is the strongest during the earrings stage, which is crucial for formation of the wheat productive process.

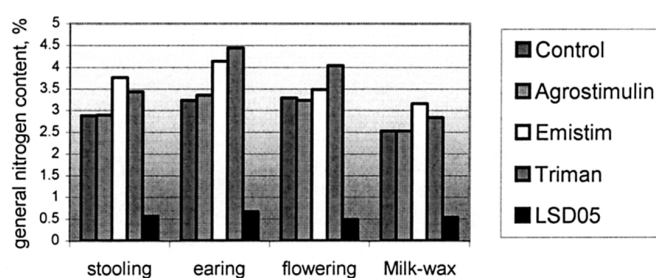


Figure 1 Influence of physiologically active substances on total nitrogen content in flag wheat leaf, % (1997)

Because regulators show cytokinin activity, they can induce the synthesis of nitrate reducing [2] regardless of the quantity of substrate and promote beginning of the synthesis of various enzymes involved into biosynthesis of RNA and proteins [3, 4]. It is known that wheat is related to an intermediate group of plants in which the nitrate reducing is allotted between roots and leaves [5]. According to our data, Agrostimulin, Emistim and Triman stimulated the increase of the level of induced nitrate reducing in the flag leaf and in its sheath particularly. Sheath, which is the leaf

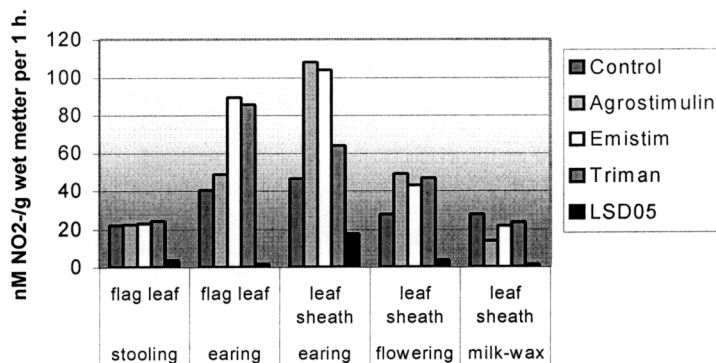


Figure 2 Influence of physiologically active substances on nitrate reductase activity (nM NO₂-/g wet matter per 1 hour) in flag leaf and sheath of winter wheat, 1998

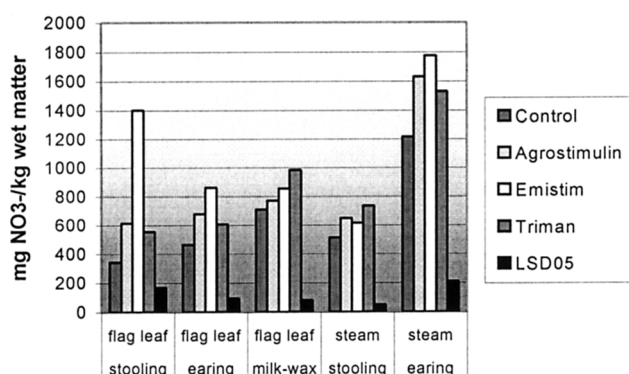


Figure 3 Influence of physiologically active substances on nitrate content in flag leaf (mg NO₃-/kg wet matter), 1997

effective among the regulators during the stage of earing (the enzyme activity increased by 132.5 %). The nitrate reducing in sheath of the Emistim-treated plants has risen by 123.6 % at the stage of earing compared to the control plants.

We also studied the nitrate content in the test plants. According to our data (Figure 3), under growth regulators' action, the nitrate content in the flag leaf grew, especially at the stage of stooling (under Agrostimulin action it grew by 79.2 % and under the action of Emistim it grew by around 400 %). This may be due to somewhat too dense sowing of wheat, which may have caused insufficient illumination of photosynthesizing organs, which, in turn, may lead to accumulation of free unassimilated NO₃⁻ ions in leaves [6]. The level of nitrates especially increased in the stems of plants at the earing stage: 1631.4 mg of NO₃⁻ per kg of wet matter due to Agrostimulin, 1773.83 mg of NO₃⁻ per kg of wet matter due to Emistim and 1215.9 mg of

NO₃⁻ per kg of wet matter due to Triman compared to the control plants. There is a direct correlation between the nitrate content in wheat stem at the stages of stooling and earing and the content of protein. Therefore, these data on the nitrate content can be used for predicting the protein content in grain [7].

We have summarized our data for the crops of 1997-1999 in the following Table 1. The increase of yields as well as the increase of protein content in grain was recorded every year between 1997-1999 for the plants treated by any of three growth regulators.

In 1998, which was a year with unfavorable weather conditions because of prolonged draught, the increase in yields was especially significant for the plants treated by

	Vegetation of 1997		Vegetation of 1998		Vegetation of 1999	
	Content of proteins, %	Yield, kg per ha	Content of proteins, %	Yield, kg per ha	Content of proteins, %	Yield, kg per ha
Control*	13.43	2980	14.02	3130	10.61	3470
Agrostimulin	14.20	3580	15.03	4270	11.37	3880
Emistim	14.30	3400	14.78	4340	11.83	3970
Triman	14.62	3550	14.50	3780	12.20	4370
LSD ₀₅		370		415		390

* – control plants, as well as test plants, were grown on the plots fertilized with ammonium saltpeter (N120P90K90)

Table 1 Influence of Agrostimulin, Emistim and Triman on the protein content of grain and productivity of winter wheat (Polis'ka 90).

basis enveloping the intercalary meristem zone, appeared to be the place of the most intensive nitrate reducing.

The most significant impact of Agrostimulin, Emistim and Triman on the nitrate reducing activity was observed in the vegetation of 1998 (Figure 2), which was characterized by high daily temperatures (daily temperature varied from 19 to 24°C, the maximum temperature reached 35°C) and moisture deficiency during the stage of earing.

As it has already been mentioned, the highest nitrate reducing was detected in sheath. Agrostimulin was the most

Agrostimulin and Emistim, which are the growth regulators of natural origin. In particular, the yield of the plants treated by Agrostimulin exceeded the yield of the control plants by 36 %. For plants treated by Emistim, the figure was 40 %. The notable increase in the quality of grain and productivity of the plants treated by Agrostimulin and Emistim may attest that these growth regulators are capable of improving the plants' ability to resist stress.

During the next years, we have carried out studies on the combined use of these growth regulators and fungicides

during the pre-seedtime treatment of the winter wheat seeds. Real possibility to reduce fundamentally (by 25% and more) the fungicide expenditure without fungicide bio-protective effect being weakened but with harvest being increased and the improved quality of harvest was demonstrated. Calculations show that only due to fungicide RoksyL cost rates reduced from 1.5 kg per 1 ton of the seeds (regulated rate) to 1 kg/t during its combined use with Emistim C (10 ml/t), which would decrease expenditures on the RoksyL purchase by 400 € per 1000 ha. If the overall area occupied by the cereals in Ukraine is 12 mln ha, the currency savings may reach 50 mln €. Except of this, there may arise necessity for additional production of 3 mln t of grain to provide the harvest increase.

Not less effective may be usage of the growth regulators in parallel with the prosecution of the phyto-sanitary treatments of the winter wheat sowings against diseases. The results of the phyto-sanitary treatment of the winter wheat against the leaf diseases suggest that Emistim C failed to worsen the Tilt (propiconazole) biological efficiency relative to the extent of farinose dew and septoriose expansion: in the variants with full-scale Tilt dose and with it being reduced by 50% the progression of the farinose dew is limited by 15% and of septorioses – by 21%. Both variants with the Emistim C usage showed statistically significant harvest increase.

Annual tests of Emistim C and Agrostimulin in various soil-climatic zones of Ukraine showed that these may improve the wheat endurance not only to diseases and pests lesions, but to the other stress factors such as drought, low temperatures, soil salinisation as well.

In conclusion, it should be said, that our results show that plants treatment by new growth regulators, especially by the growth regulators of natural origin, promotes

increase in the grain yield and quality, improves adaptive abilities of wheat by enhancing the activity of nitrate-reducing system, which is proved by increase in the grain protein content, as well as favor the decreased fungicide amounts used (by 25%) during the pre-seedtime treatment of the winter wheat seeds, and is effective with simultaneous prosecution of the wheat phyto-sanitary treatments against the leaf diseases.

The usage of ecologically safe growth regulators as a means of biologization of new technologies in order to increase the grain culture productivity and extend the employment of new kinds of biological approaches to plant protection, especially in unfavorable environment conditions, is very urgent in modern sustainable agriculture.

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PERSISTENT ORGANOCHLORINE RESIDUES IN SUBCUTANEOUS BLUBBER OF MARINE TUCUXI, *Sotalia fluviatilis* (CETACEA, DELPHINIDAE), FROM RIO DE JANEIRO STATE, BRAZIL – PRELIMINARY RESULTS

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INTRODUCTION

Cetaceans are top marine predators and have been shown to bio-accumulate high concentrations of persistent organochlorines. As such, they can integrate both temporal and spatial variations in environmental contamination (O'Shea, 1999).

The marine ecotype of tucuxi dolphin (*Sotalia fluviatilis*) occurs in coastal waters from Honduras, Central America, to Santa Catarina, Southern Brazil (Da Silva & Best, 1996;

Rio de Janeiro State, Brazil. This bay is surrounded by a metropolitan complex with more than 11 million inhabitants, bordered by more than 6,000 additional industries in the drainage basin (Perrin et al., 1997). It is very affected by the destruction of mangroves, over-fishing, harbor activities, constant oil spills, metals waste impacts, organochlorines and butyltins (JICA, 1992; Fernandez, 2001).

This study presents the preliminary results of an investigation into the concentrations of organochlorines (DDTs and PCBs) in the blubber of the marine tucuxi, *Sotalia fluviatilis*, in the most degraded zone of Brazilian coast.

MATERIAL AND METHODS

The blubber samples of marine tucuxi (n=6) were collected from specimens caught accidentally by fishermen and stranded in Rio de Janeiro State (Table 1).

After dissection, all samples were wrapped in aluminum foil and preserved at - 20°C, until the moment of the analysis (Geraci & Lounsbury, 1993).

About 1,0 g of blubber samples were homogenised with anhydrous Na₂SO₄ and extracted by continuous Soxhlet apparatus, using a modified hot soxhlet for 2 hours with a mixture of cyclo-hexano:n-hexano:isooctane (15:5:2). An aliquot (1mL) was mixed with sulphuric acid for the clean-up. After centrifugation and phase separation, an internal standard (octachloronaphtalene) was added for the quantification. The lipid content was measured gravimetrically. A Shimadzu GC-14B with a ⁶³Ni electron capture detector (ECD) was used in the analysis. Organochlorine concentrations are expressed as µg/g wet weight calculated on a lipids basis (ug/g lipid wt.).

Specimen Number	Sex	Total Length (cm)	Locality
1	F	73	Praia de Cambinhas, Niterói
2	F	185	Barra de Guaratiba, Rio de Janeiro
3	F	198	Praia Costa Azul, Rio das Ostras
4	M	191	Baía de Guanabara
5	F	189	Conceição de Jacaré
6	F	125	Baía de Guanabara

Table 1: The main characteristics of specimens collected from Rio de Janeiro State.

Simões-Lopes, 1987). The coastal habits expose the tucuxi dolphin to a large variety of environmental problems, related with the increase in human population along the Latin American coast.

The tucuxi is a top predator in coastal areas and its have a high residence pattern in bays and estuarine systems and an extend life span, c.a. 30 years (Ramos, 1997; Flores, 1999; Santos et al., 2001; Pizzorno, 1999; Cunha, 1999). Thus, this species could be used as an indicator of the biomagnification processes along Latin America Atlantic coast. Even so, few studies have been made to accomplish the picture of the contamination of this species (e.g. Koeman et al., 1972; Lailson-Brito, 2000; Lailson-Brito et al., 2002).

One area with a population of *Sotalia* gathers all the characteristics described above, namely the Guanabara Bay,

RESULTS AND DISCUSSION

The results are summarised in Table 2. The PCBs and ΣDDT concentrations ranged between 0,11 – 7,65ug/g and 0,05-5,42ug/g, respectively. PCBs concentrations were higher than ΣDDT. The PCB with higher concentration in all samples was PCB – 153 (Figure 2).

The ΣDDT/PCBs ratio ranged from 43 to 70 %, indicating higher industrial pollution. In general, the organochlorine concentrations were considered low, when compared to another cetacean population from the Northern hemisphere (Reijnders et al., 1999).

Even so, the analysis of an animal (Specimen Number 4) was re-done using a new extraction method (by continuous Soxhlet apparatus, using a modified hot soxhlet for 6 hours with a mixture of hexane:dichloromethane 1:1) and the

Specimen Number	Lipid content (%)	Σ DDT	Σ PCB	Σ DDT/ Σ PCB(%)	DDE/DDT(%)
1	80	0.76	1.50	51	44
2	76	5.42	7.65	71	31
3	94	0.05	0.11	43	59
4	67	0.99	1.74	57	69
5	78	0.41	0.92	45	57
6	81	1.05	2.16	49	60

Table 2: Concentrations of organochlorines (mg kg⁻¹ lipids basis) in the blubber of marine tucuxi dolphin from Rio de Janeiro State.

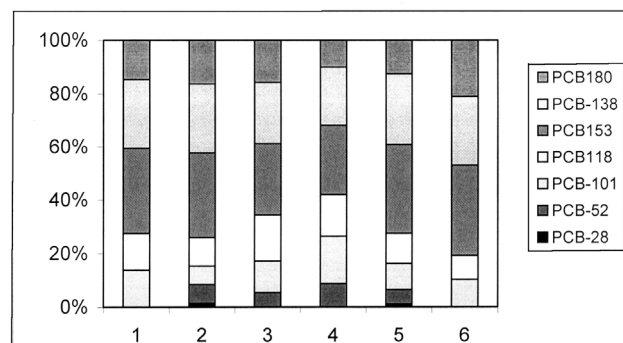


Figure 1: Contribution of PCB congener in blubber's samples for each tucuxi dolphin.

Specimen	Lipid content (%)	Σ DDT	%DDE	Σ PCB	DDT/PCB
4	66.07	32.27	85.83	64.20	0.50

Table 3: Concentrations of organochlorine in blubber (mg kg⁻¹ lipids basis). Analysis of an animal (Specimen Number 4) re-made using a new extraction method.

concentrations turned out to be much higher as regards the contents of PCBs and DDTs (Table 3).

These new results show high concentrations, similar to the organochlorine concentrations in cetaceans of contaminated areas of the Northern Hemisphere (Reijnders et al., 1999). Therefore, all the analyses will be re-done to verify the real status of the contamination for organochlorines compounds in the cetaceans of the State of Rio de Janeiro.

The marine tucuxi only feeds on fish and squids (Di Benedetto, 2000). Studies focusing on the flow of organochlorine throughout the cetacean's food chain are essential. Further studies focusing on organic compounds with larger sample sizes, including other marine tucuxi populations, are urgently required for a better understanding of the significance of organochlorine accumulation in these species throughout their life cycle.

ACKNOWLEDGEMENTS

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TOTAL MERCURY AND ORGANIC MICROPOLLUTANTS IN TOP MARINE PREDATORS

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INTRODUCTION

Environmental degradation is becoming more apparent day by day, not only near the big cities, but also in isolated areas and protected environments far from human activities.

The increasing pollution is reaching global proportions, reflected not only by the greenhouse effect, climate change and contamination of atmosphere, oceans, soils and rivers with persistent pollutants (e.g. organochlorines and mercury), that present cumulative toxic effects upon the organisms (Mackay D. et al. 1995).

Sharks like *Prionace glauca* and *Carcharinus falciformis* and teleosts fish like *Xiphias gladius* are top predators and represent important sources of protein, largely consumed in Brazil, and are also export products with great commercial value, specially on the American market. However, such species located at the top of the food chain may accumulate high levels of persistent pollutants and become highly dangerous to human beings (e.g. pregnant women).

In this report we present analytical results of the total mercury (THg) concentrations in muscle tissue of the blue-shark (*Prionace glauca*) and in the teleost fish *Xiphias gladius* and PCB and organochlorinated pesticides in *Charcharinus falciformes*.



Figure 1: *Prionace glauca* (Linnaeus, 1758)

Popular Name: Blue-shark; Family: Carcharinidae; Order: Carchariniiformes; Class: Elasmobranchii; Maximum length: 400 cm; Maximum weight: 206 kg; Habitat: marine pelagic habits, in depths from 0 m to 350 m, both temperate and tropical regions; Feeding habits: the main food is teleost fish, other small sharks, skids, pelagic crustaceans, occasionally marine birds and floating debris.



courtesy Virginia Institute of Marine Science

Figure 2: *Xiphias gladius* Linnaeus, 1758

Popular name: swordfish; Family: Xiphiidae; Order: Perciformes; Class: Actinopterygii; Habitat: oceanic and cosmopolite, an epi and mesopelagic fish, present in tropical and temperate waters of all oceans. It is present in all Brazil's coastal zone; Biology: Presents a wide thermal tolerance, from 5° to 27°C; occurring from the surface until depths greater than 600 m. The females grow faster than males, and are somewhat bigger in terms of maximum length.



Figure 3: *Carcharinus falciformis* (Bibron, 1839)

Family: Carcharhinidae; Order: Carcharhiniiformes; Class: Elasmobranchii; Habitat: Found in oceanic as well as coastal areas (prefer temperatures between 23o to 24oC. Occurs from the surface until less than 500 m; Feeding habits: Preference is pelagic fish; Biology: Viviparous species presenting a kind of viteloin placenta with 2 to 14 'babies' per time. Its average length is 200 to 240 cm, with a maximum around 330 cm.

MATERIALS AND METHODS

Method for organochlorines:

One gram freeze-dried tissue was extracted in hot Soxhlet (90°C / 2h) using hexane:cyclohexane (3:1) + isooctane. The extract was evaporated and digested conc. H₂SO₄ and centrifuged (3000 rpm/15min), the top layer is injection on GC-ECD (Shimadzu 14B)

Method for total Hg:

N = 34 *P. glauca*, 20 *X. gladius*. 0,4g muscle tissue is digested using 1 mL H₂O₂ and 3 mL H₂SO₄: HNO₃ in a hot bath 60°C / 2h. After cooling there is another oxidizing step with 5 mL KMnO₄ 5%. After reduction using 1 mL NH₄OCl + NaCl 12% and 10 mL H₂O Milli-Q the sample is sent to cold vapour atomic absorption spectrometry (CVAAS), with automatic flow injection system (FIMS-400 Perkin-Elmer)

SAMPLING AREA

The analysed specimens were collected at the central east coast of Brazil, by the REVIZEE Program (Program of Live Resources of the Exclusive Economic Zone) during the operation central 6.

A preliminary analysis of organic micro-pollutants reveals a considerably high contamination with Sum of PCBs = 212,26 ng.g⁻¹ and Sum of DDT = 44,95 ng.g⁻¹ (Graf.6)

RESULTS

The species *P. glauca* and *X. gladius* presented a somewhat homogeneous pattern among different lengths (mean *glauca* = 238 cm; min *glauca* = 211 cm and max *glauca* = 273 cm; mean *gladius* = 189 cm; min *gladius* = 106 cm e max *gladius* = 275 cm), indicating that the sampling was uniform for this parameter. The same was observed in terms of the weight (Figure1 and 2).

Both species presented similar trends of THg, with a normal distribution of this contamination (Graf. 3). The species presented significant differences ($p < 0,05$) in its THg concentrations in the muscle tissue when the Student T-test is used ($t = 3,17368$, $t_{tab} = 3,1737$; $gl = 19$ e $p = 0,00500$).

In six samples of *P. glauca* and one of *X. gladius* the concentration observed surpassed the regulatory limits of the Brazilian legislation (ANVISA), which is 1 ng.kg⁻¹ (wet weight).

The regression coefficients between [THg] X weight was 0,3569 and 0,5335 to *P.glauca* e *X. gladius* respectively (Figure 4 and 5).



Figure 4: Study Area

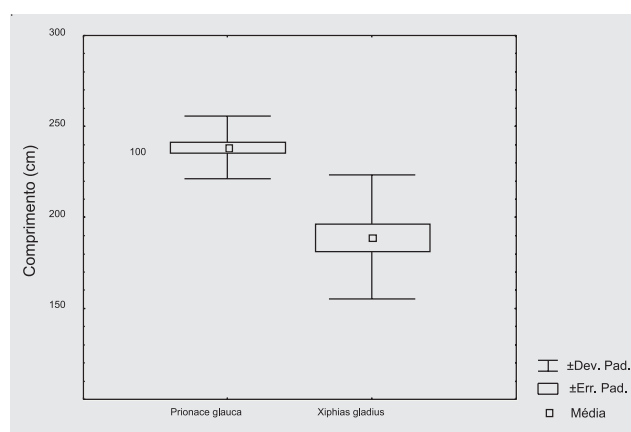


Figure 5: Comparison of length of the species

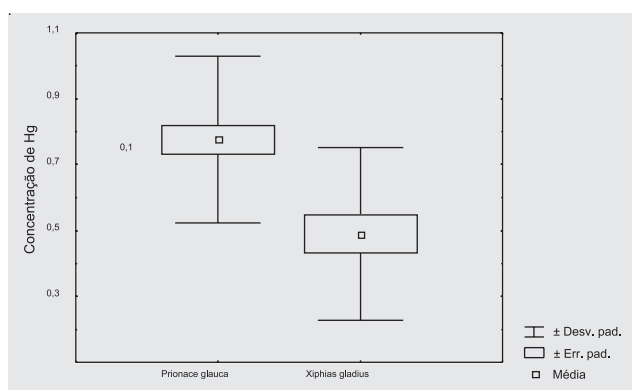


Figure 6: Comparison of weight of the species

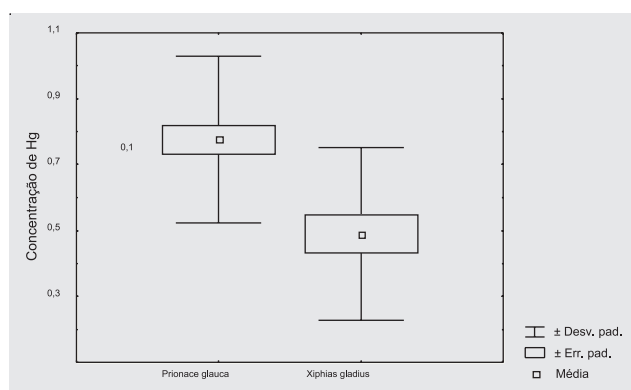


Figure 7: Comparison of THg content of the species

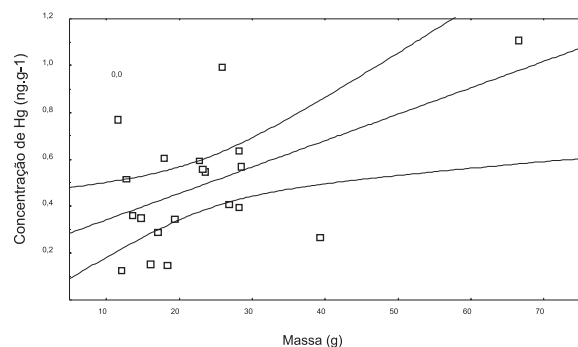


Figure 8: Correlation between the concentration of THg and the mass of *X. gladius* specimen ($y = 0,32983 + 0,00751 * x$, $r = 0,5$).

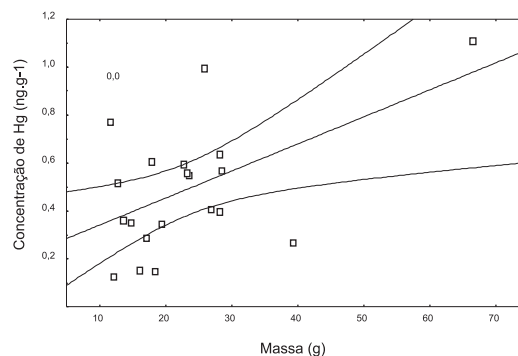


Figure 9: Correlation between the concentration of THg and the mass of *P. glauca* specimen ($y = 0,22857 + 0,01127 * x$, $r = 0,5$).

CONCLUSIONS

- The concentrations of Hg in both species presented a normal distribution of the data taking in account the total length and weight of the fish.

- According to the legal limit of ANVISA (1 ng.kg⁻¹ w. w.) is represents a 76g/day for *P. glauca* and 122g/day for *X. gladius*, using the WHO guideline (0,5 ng.kg⁻¹ w. w.) one should consume half of these values.

- The preliminary results of organic micro-pollutants opened a new research line for the laboratory and now all of the samples are going to be analysed.

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EVALUATION OF SELECTED PESTICIDES BY INSTRUMENTAL, IMMUNOANALYTICAL METHODS AND AQUATIC ECOTOXICITY BIOTESTS

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ABSTRACT

Water polluting pesticides present a continuous risk to aqueous ecosystems; therefore, effective analytical and bio-analytical methods are required to monitor their presence and toxicological effects. In the scope of a monitoring program, analytical and bio-analytical methods were developed and applied to monitor selected target analyte pesticides in water. Analytical methods developed included instrumental analysis i.e., gas chromatography - mass spectrometry (GC-MS) and immuno-analysis i.e., enzyme-linked immuno-sorbent assays (ELISAs). Bio-

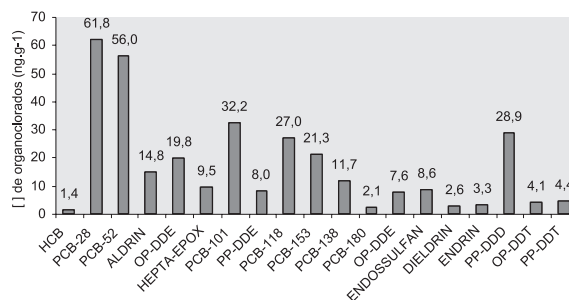


Figure 10: Organochlorines in *C. falciformis* (n=1).

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analytical methods included the use of a standardized aquatic toxicity test using *Daphnia magna* (Straus) as an indicator organism and the development of a related instrumental analytical method detecting changes in the level of exo-metabolites by *D. magna* on the basis of a chemo-luminescent signal. The advantage of the analytical methodology is that an accurate picture can be achieved on the presence of a given contaminant. Biological monitoring methods, on the other hand, provide information on the toxicity of the parent analyte and its metabolites in the given matrix. To obtain a detailed view on the contamination and its eco-toxicological consequences, analytical and bio-analytical methods are to be used in parallel.

In the present study, three pesticides were chosen as model compounds for monitoring: methomyl, a traditional carbamate type insecticide acting by inhibiting normal neural signal transduction; fenoxycarb, an insect growth regulator acting as an insect juvenile hormone agonist; and the herbicide trifluralin of strong endocrine disrupting effects. Contaminating levels of the selected compounds were verified by GC-MS and/or ELISA methods in spiked water samples in the concentration range of 1 – 6400 ng/ml. Solid phase extraction (SPE) was applied for sample preparation prior to GC-MS, while water samples were subjected directly to ELISA. In parallel, the toxicity of these aqueous samples to *D. magna* was detected by the 48-hr immobilization test according to the corresponding

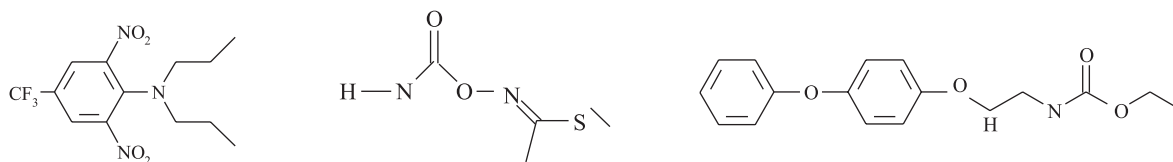


Figure 1: The Chemical Structure of the Three Analytes: Trifluralin, Methomyl and Fenoxycarb.

ISO protocol. In addition, a chemo-luminescent test on *D. magna* was carried out detecting the changes in the level of exo-metabolites at 1, 2 and 24-hrs post treatment. *D. magna* individuals were placed in artificial nutrient medium in both cases. .

Ecotoxicity studies indicated that the highest toxicity on *D. magna* was induced by methomyl, where all the subjected individuals died 2 hrs after treatment at 160 ng/ml. Trifluralin displayed an apparent lethal concentration LC50 above 220 ng/ml, with detectable reduction in the metabolism after only 1 hr post treatment. In contrast, fenoxycarb caused significant reductions in the metabolism of *D. magna* only at concentrations above 800 ng/ml; nonetheless, increasing mortality was seen with this compound after 48 hrs attributed to molting abnormalities due to hormonal effects. An advantage of the instrumental chemo-luminescent *D. magna* test developed at the Ukrainian laboratory is that changes in the metabolism of the subjected animals can be seen as early as 1 hr after treatment. The present work has demonstrated the utility of the parallel use on analytical and eco-toxicological tests for evaluation of water contaminating pesticides.

INTRODUCTION

In the scope of our ongoing efforts to identify, detect and monitor potentially water-contaminating pesticides in the environment, we have (A) compiled a list of presently registered compounds posing environmental/eco-toxicological/human toxicological risk; (B) developed and continue to develop analytical and bio-analytical methods for the detection of these toxicants and (C) carry out systematic monitoring or toxicity evaluation campaigns. Among a list of selected pesticides, three active ingredients were selected for the present study based on ecotoxicological considerations: the herbicide trifluralin and two insecticides, methomyl and fenoxycarb (Figure 1). The dinitroaniline derivative trifluralin is a rather old herbicide (introduced in 1960), which has been found to exert considerable ecotoxicity, among others and it has been enrolled in the EU list of proven endocrine disrupters (Commission of the European Communities, 2001). The carbamate compound methomyl is also an old fashioned insecticide (introduced in 1967) acting by inhibiting acetylcholinesterase, therefore potentially affecting all species with nerves or a nervous system, and has been classified as Restricted Use Pesticide (RUP) by the US Environmental Protection Agency due to its high acute toxicity to humans (Tomlin, 2000). In contrast, fenoxycarb is a novel, insect growth regulator (introduced in 1985) acting as an insect juvenile hormone analog, applied in Integrated Plant Management

(IPM) practices e.g., for insect control in orchards. The first two analytes are of ecotoxicological concern due to their acute toxic effects; therefore, they are subjected to limitation or restriction on their use. Moreover, due to its absorbance and slow decomposition in soil, trifluralin is a potential water contaminant. In contrast, fenoxycarb is more an environmentally friendly pesticide, yet it exerts hormonal action on arthropods in aquatic ecosystems, and possibly due to its high lipophilicity it is somewhat persistent in the environment.

MATERIALS AND METHODS

Instrumental analysis: GC-MS analyses were carried out on a Saturn 2000 workstation (Varian, Walnut Creek, CA, USA) by injecting the above pesticides in isooctanic solutions. GC-MS conditions were as follows: fused-silica column CP-Sil 8 CB, 0.25 mm film thickness, 30m x 0.25 mm I.D.; injection mode splitless; injection volume 5 ml; injection temperature programmed from 60°C (held for 0.5 min) to 260°C at a rate of 200°C/min, and the final temperature was held for 5 min; column temperature programmed from 70°C (held for 0.5 min) to 100°C at a rate of 60°C/min and then to 240°C at a rate of 10°C/min and the final temperature was held for 20 min. Helium was used as carrier gas, pressure 0.097 MPa; ionization current 350 mA; electron energy 70 eV. The iontrap was scanning in EI-mode from 40 to 650 amu. The selected ions for quantitation were 264 and 306 amu for of trifluralin, 88 and 116 for fenoxycarb, and 58 and 105 for methomyl (quantitation ions are listed underlined).

For GC-MS analyses, water samples were spiked with the target analytes at concentrations between 0.25 and 25 ng/ml, and were subjected to solid phase extraction (SPE). Thus, water samples were filtered to remove suspended particles, stirred for 1 min and let stand for 10 min. Carboxprep-90 columns (500 mg, 6 ml, Restek, Bellefonte, PA, USA) were placed on a vacuum suction manifold, and were conditioned by slow passage of 5 ml of a mixture of dichloromethane and methanol (8:2), 2 ml of methanol and then 15 ml of a 10 g/l solution of ascorbic acid in distilled water through them against reduced pressure. Then, 1000 ml of each water sample was loaded onto the conditioned Carboxprep-90 columns with a flow rate of 10-15 ml/min. The columns were rinsed with 7 ml distilled water, remained under suction against air for 10 min to reach air dryness, then rinsed with 1 ml of a solution of methanol and distilled water (1:1), and again remained under air suction for 10 min. Non-acidic contaminants concentrated on the column were eluted with 1 ml of methanol, followed by 6 ml of a mixture of dichloromethane and methanol

(8:2) using a low flow rate of 2 ml/min. Each combined elute was concentrated under nitrogen to approximately 0.2 ml, 2 ml of isooctane was added, and the solutions were concentrated to 1 ml final volume.

Immunoassay: Previously developed in-house enzyme-linked immunosorbent assays (ELISAs) were used to detect trifluralin and fenoxycarb (Hegedűs *et al.*, 2000, Le *et al.*, 2003, Székács *et al.*, 2003a, 2003b). ELISAs were carried out in high capacity 96-well microplates (Nunc, Roskilde, Denmark, #442404), and were read in an iEMS microplate reader (LabSystems, Helsinki, Finland). Microplates were coated by incubating at 4°C overnight with 100 µl per well of a BSA conjugate of the analyte as coating antigen in 0.1 M carbonate buffer (pH=9.6). After washing with 0.01 M phosphate-buffered saline (0.8% NaCl), pH 7.4 (PBS) buffer, plates were blocked by incubation at 38°C for 1 h with 150 µl per well of blocking agent (1% gelatin in PBS, pH=7.4). After washing the microplate wells with PBS containing 0.2% Tween 20 (PBST 0.2) in a manual plate washing device, 50 µl per well of standards or samples and 50 µl per well of antisera diluted in PBS containing 0.2% Tween 20 (PBST 0.05) were added, and plates were incubated at 38°C for 60 min. After an additional wash with PBST 0.2, 100 µl per well of goat anti-rabbit IgG-HRP conjugate (BioRad Laboratories, Hercules, CA, USA) at a dilution of 1:12,000 in PBST 0.05 was added, and incubated for 60 min as before. After a final washing step with PBST 0.2, 200 µl per well of the substrate solution (1.2 mM H₂O₂ with 3 mM 1,2-phenylenediamine (OPD) in 200 mM potassium dihydrogen citrate buffer, pH=3.8) were added. Upon sufficient color development (after 10 to 60 min) the enzymatic reaction was stopped by the addition of 50 µl per well of 4 N H₂SO₄. Color intensities in the wells (endpoint mode) were read at 492 nm.

Standard curves from the raw data were calculated using four-parameter (sigmoid) equation. The LOD was defined as the analyte concentration, causing a decrease of three standard deviations from the blank standard absorbance (a mean of at least three replicates).

Aquatic biotest: Aquatic biotests carried out are to detect what effects the three selected active ingredients on the non-target aquatic ecosystems exert. Because the mobility test on *D. magna* Straus (Cladocera, Crustacea) is an obligatory test in pesticide registration (ISO, 1996), this test was used first to characterize aquatic toxicity. In parallel, an instrumental method developed at the Palladin Institute of Biochemistry of the Ukrainian National Academy of Sciences was carried out, based on chemoluminescence determination, detecting metabolism rate in *D. magna*.

Methanolic solutions of the pesticides were tested on *D. magna* as test animals. Aquatic toxicity tests were carried out according to the 48-hour immobilization test ISO protocol where 5 individuals were placed into 10 ml of artificial medium (buffer containing CaCl₂, KCl, MgSO₄ and NaHCO₃ salts). To obtain further data, the subjected ani-

mals received dry yeast as feed after 48 hours, and tests were continued to 96 hours. Each treatment was carried out in 4 replicates. An additional test based on chemoluminescence determinations was carried out. In that test, changes in the levels of *D. magna* exometabolites were investigated by a luminometer (HML 3 instrument with FEP 176 photoelectron multiplier) 1, 2 and 24 hours after treatment. The instrument detects peroxidase activity attributed to excreted metabolic products by *D. magna* in the test medium, with the use of hydrogen peroxide as a substrate and luminol as a chromophore. Due to peroxidase activity, hydroxyl and superoxide radicals liberated from hydrogen peroxide oxidize luminol to the excited state luminol-dioxide, and this substance is auto converted to 3-amino-phthalate with the emission of a 425-445 nm photon (i.e., chemoluminescent signal). The luminometer detects the intensity of the emitted photons in quanta/sec. The sensitivity of the instrument is 10⁵ sec/sec, thus only counts over this limit were detectable.

RESULTS

Instrumental analysis. (GC-MS): Using the above GC-MS conditions, trifluralin was readily detected with a retention time (Rt) of 10.9 min, and the detection limit (LOD) was 0.001 mg/ml (in isooctane). Fenoxycarb gave a clear sharp peak at 21.2 min (21.06-21.42 min) with an LOD of 2.5 mg/ml (in isooctane). In contrast, methomyl provided a weak peak over 15 min at 5 mg/ml (in isooctane) (Figure 2).

Detectability of these analytes by GC-MS is a function of substance volatility: the outstanding volatility of trifluralin allows its superior LOD, while fenoxycarb was barely detectable, while methomyl was undetectable at 2.5 and 5 mg/ml, respectively. (The Henry constants of the three compounds are 15, 3.3×10⁻⁵ and 2.13×10⁻⁶ Pa·m³/mol, respectively.)

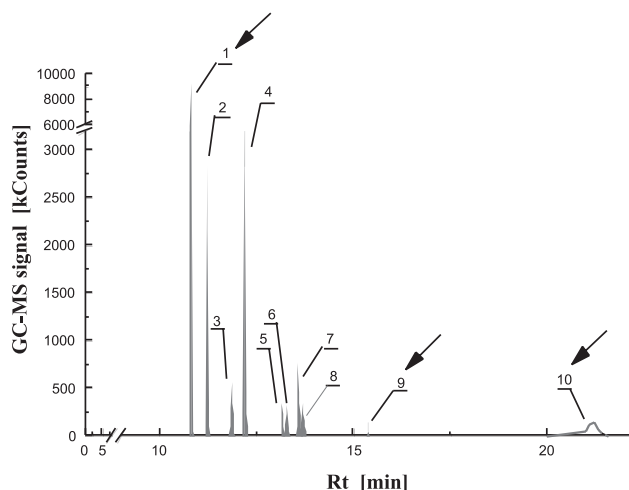


Figure 2: GC-MS Chromatogram of the Selected Pesticides. Arrows Indicate the Three Analytes, Trifluralin, Methomyl and Fenoxycarb.

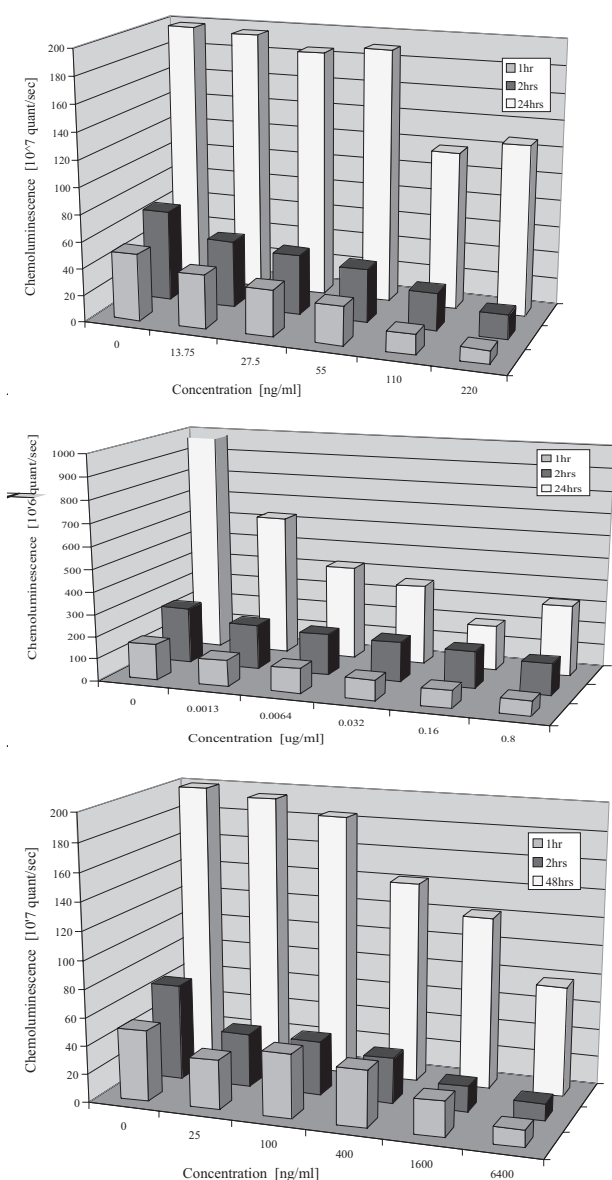


Figure 3: Concentration Dependence of the Chemoluminescent Signal in the *D. magna* Luminometric Assay with the Three Analytes: Trifluralin (left), Methomyl (right) and Fenoxycarb (middle)

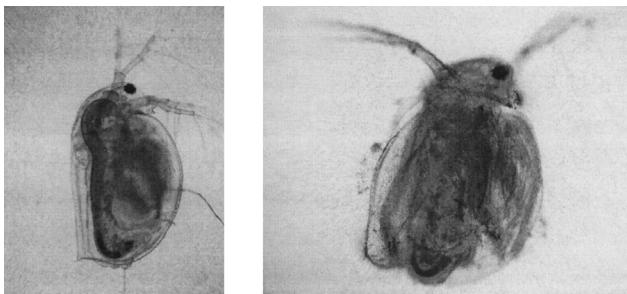


Figure 4: Developmental Abnormalities in *D. magna* Due to Hormonal Interaction with the Analyte (Left: Normal Individual, Right: Irregular Cuticle Formation).

Immunoanalysis (ELISA): ELISA systems, developed at the Plant Protection Institute of the Hungarian Academy of Sciences, detected trifluralin and fenoxycarb in the 0.1–100 ng/ml range, with IC_{50} values of 2.87 ± 0.39 and 2.7 ± 1.6 ng/ml, and LODs of 0.8 and 0.11 ng/ml, respectively. No ELISA system for the detection of methomyl was available. The two ELISA systems readily detected trifluralin and fenoxycarb in water samples, and ELISA detection was validated by GC-MS.

Aquatic biotest on *D. magna*: Aquatic 48 hrs immobilization biotests revealed toxicity of the target analytes to *D. magna* in the 5–900 ng/ml concentration range (Figure 3). Methomyl showed toxicity at 20–50 ng/ml, while the other two analytes exerted toxic effects in the 200–500 concentration range. This is in good agreement with LC_{50} values reported by Tomlin, 2000 as LC_{50} s (48 hrs) of 31.7, 245 and 400 ng/ml for methomyl, trifluralin and fenoxycarb, respectively.

Using fenoxycarb, with incubation times over 96 hrs showed certain mortality (or cessation of mobility). Such delayed action is typical for hormonal activities, thus it is assumed that although the hormonal system of crustaceans differ from that of insects, this pesticide disturbs the hormonal system of *D. magna*.

Luminometric testing of the three active ingredients was successful. Increased photon emission was recorded at low doses (0.625 mg/ml), while clear hyperactivity was occasionally seen even with a naked eye which was recorded with certain subjected individuals as rapid irregular movement. Detectable metabolism was decreased by increasing analyte concentrations in the range (5–10 mg/ml) by a lesser degree in the first 2 hrs, and by 50% decrease after 24 hrs, which gave a hint of subsequent mortality. Thus, for substances of known photochemical activity, the chemoluminescent aquatic toxicity test method was proven useful, rapid and sensitive.

With certain treatments with fenoxycarb and similar hormonally active compounds, morphological changes, considered as molting abnormalities, in the subjected animals were also recorded (Figure 4). The cuticle layer around the affected *D. magna* individuals appeared irregular and seemed to be multi-layered under the microscope.

A problem with the luminometric evaluations is that a matrix effect was seen with plant extract samples: extracts absorbed photons (in spite of the fact that pigments and other color substances were removed during sample clean-up), and therefore, it seemed that reduced metabolic activities were recorded regardless the true effect of the treatment. Photon absorbance rate was proven to be concentration dependent, misleading to erroneous conclusions. At the present state of the evaluation it was believed that the extracted peroxides or chlorophyll content (also of certain peroxidase activity) might be responsible for this matrix effect. Another possibility is that free peroxide content of the plant extract, or the presence of aldehydes or ketons (verifiably interfering with the chemoluminescence of luminol) may affect the signal. Thus, the method based on chemoluminescence detection is not valid for testing substances of uncertain composition and effects, and it can be

applied solely after full characterization and elimination of possible matrix effects (as in the case of all such method developments). Yet in simple matrices i.e., in surface water, the instrumental biotest was fully applicable and prove its utility in environmental analysis.

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ORGANOCHLORO COMPOUNDS IN AQUATIC SEDIMENTS OF THE REPUBLIC OF MOLDOVA

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ABSTRACT

Organic contaminations, including PAHx and DDX compounds, were determined in aquatic sediments in order to establish the impact on agriculture (fruit-growing) from contamination. Test sampling was performed depending on the type of agroecosystems, the position of artificial lakes (so-called anti-erosional) and the contamination expected. In addition the different sediments (border/center of the lake) were sampled. The total concentration of $\Sigma 16$ HAPs is small. The results differ much depending on the sediment type (river/lake) and place of sediment (border/center of the lake). The sum of PAHs is in a range of 428,88 ug/kg d.m (river Ciuhur), 59,64 ug/kg d.m (center of the lake Colonita), 17,05 ug/kg d.m (border of the lake Colonita) and 50,4 ug/kg d.m (lake placed in the forest ecosystem, comparatively far from agricultural fields). DDX compound (DDT and its metabolites) show high concentration (49,76 ug/kg d.m (border) and 69,33 ug/kg d.m (center) of the lake, which indicate a widespread use of this insecticide and can be used as indicators of the level of pollution in aquatic sediments. p-p'-DDE is the dominant metabolite in sediment samples (44,40 ug/kg d.m (border) and 20,39 ug/kg d.m (center) of the lake. DDX compounds (DDT and its metabolites) show high concentration

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(49,76 ug/kg d.m. – border and 69,33 ug/kg d.m. – center of the lake), which indicate a widespread use of this insecticide and can be used as indicators of the level of pollution in aquatic sediments. p-p'-DDE is dominant metabolite in sediment samples (44,40 ug/kg d.m. – border and 20,39 ug/kg d.m. – center of the lake). Quotation of p-p'-DDE (40%) prevails under p-p'-DDD (20%).

Generally the PAHs and chloropesticides contamination of aquatic sediments shows an impact of these POPs on the environment as a "result" of their massive (sometimes unjustified) utilization in the agriculture of the Republic of Moldova.

Key words: aquatic sediments, contamination, PAH, organochlorine pesticides.

INTRODUCTION

In contrast to many naturally occurring compounds, as constituents of the Earth's crust, for example heavy metals, the majority of persistent organic compounds are not present naturally in significant amounts (Naumann, 1994).

Many organic pollutants are susceptible to dispersion on a regional and global scale, because they are both persistent in the environment and have a volatility that enables them to move between the atmosphere and Earth's surface in repeated, temperature-driven cycles of deposition and evaporation (Wania and Mackay, 1995). In this way all terrestrial ecosystems and other surfaces (aquatic ecosystems) receive an input of semi-volatile organic compounds from the atmosphere or as direct (i.e. pesticides) deposition and once deposited may reside in their components for many years. Therefore we cannot speak of geochemical back-

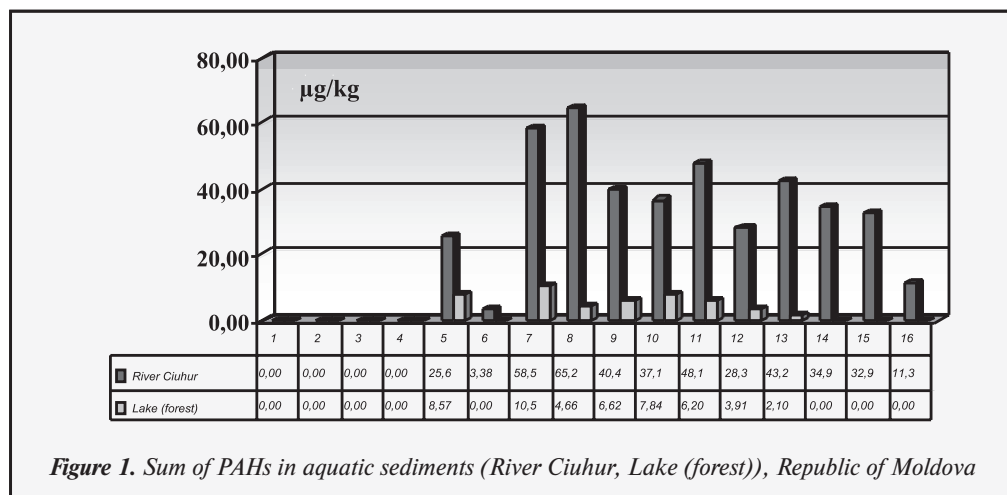


Figure 1. Sum of PAHs in aquatic sediments (River Ciuhur, Lake (forest)), Republic of Moldova

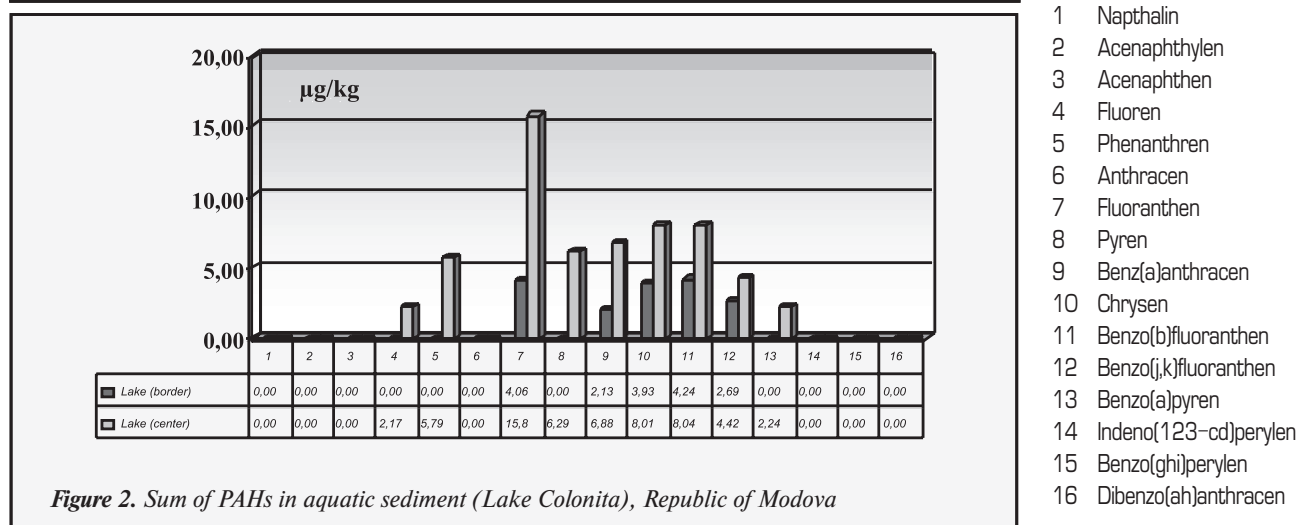


Figure 2. Sum of PAHs in aquatic sediment (Lake Colonita), Republic of Moldova

- 1 Naphthalin
- 2 Acenaphthylen
- 3 Acenaphthen
- 4 Fluoren
- 5 Phenanthren
- 6 Anthracen
- 7 Fluoranthren
- 8 Pyren
- 9 Benz(a)anthracen
- 10 Chrysen
- 11 Benzo(b)fluoranthren
- 12 Benzo(k)fluoranthren
- 13 Benzo(a)pyren
- 14 Indeno(123-cd)perylene
- 15 Benzo(ghi)perylene
- 16 Dibenzo(ah)anthracen

ground values in the context of these organic compounds. Every amount of these POPs found in the components of ecosystems (soils, plants, sediments etc.) indicates the general anthropogenic impact.

In order to establish the impact on agriculture (fruit-growing) from the contamination of the environment and to define background values of organochloro compounds, the poly-cyclic aromatic hydrocarbons (PAHs) and some of the persistent chlorinated organopesticides, such as DDX-group (o, p – DDE, p, p' – DDE; o, p' – DDT; p, p' – DDT; o, p' – DDD, p, p' – DDD) in aquatic sediments (border/center of the lake and river) were analyzed.

Polycyclic aromatic hydrocarbons (PAH) represent an important class of contaminants because of their widespread distribution in the environment and their toxic properties. The contamination of the environment by PAHs occurs mostly as a result of human activities and by natural processes (Shegunova, 2002).

Organochlorine compounds have been particularly effective in control of pests and diseases, but their resistance to degradation has resulted in them being universal contaminants in terrestrial and aquatic ecosystems. In spite of the fact that utilization of organochloro pesticides in the Republic of Moldova has been prohibited long ago (DDT was forbidden in 1970) and their abundant application was provided that

DDX compounds are present in agricultural soils, their concentration amplitude is high (in the soil layer (0–60 cm) collected from the territory of storage site for chemicals, very high – 16592 ug/kg) (A. Târîtă, 1995). As the surface layer of agricultural soils is mostly contaminated with DDX compound and is also the first to be removed by erosion, it means that the transported sediment and the transporting water can be enriched in such pollutants. Although pollutants are transported by water systems, sediments reflect the physicochemical and ecological status of the waters. Sediments act as natural buffer and filtration system in the terrestrial – limnological cycle in particular. The aquatic sediments from lakes placed between agrocenoses can represent an integration of the contaminants emitted over time and may be used as an indicator of local and short-term inputs.

MATERIALS

Extraction

The samples (not previously dried) were mixed with Na₂SO₄ and extracted with hot toluene in Soxtec apparatus.

Clean-up

Clean-up of the sediment extract was performed by:

- Gel chromatography on Biobeds S – X3 and
- Adsorption chromatography on silicagel and silicagel/AgNO₃

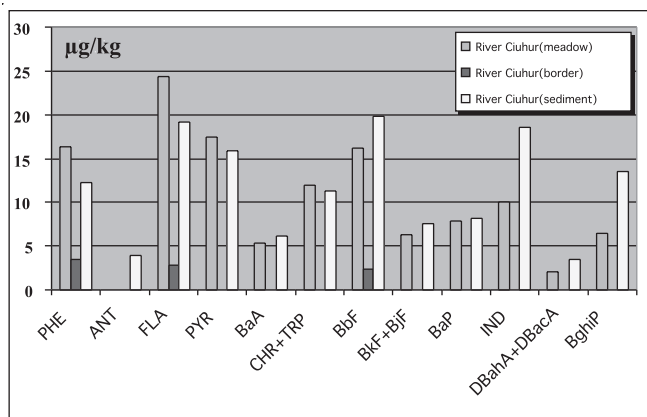


Figure 3. Distribution of individual PAH compounds in soil (0--20 cm) and aquatic sediment, Republic of Moldova

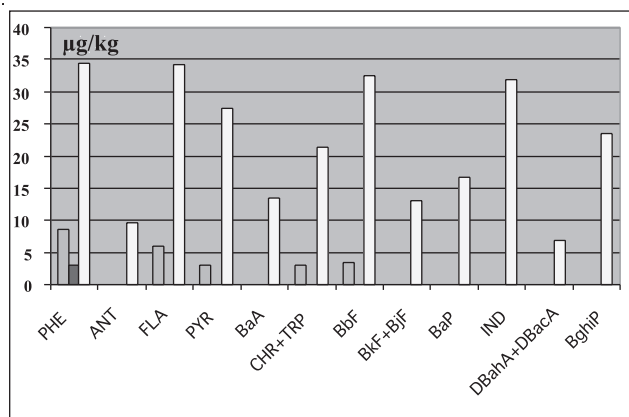


Figure 4. Distribution of individual PAH compounds in soil (20--40 cm) and aquatic sediment, Republic of Moldova

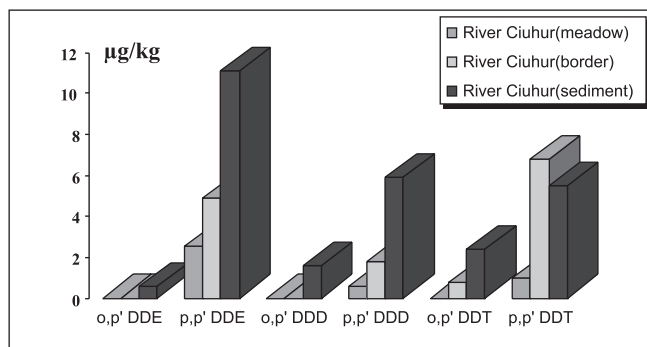


Figure 5. DDX compounds in soil (0--20 cm) and aquatic sediment r. Ciuhur, Republic of Moldova

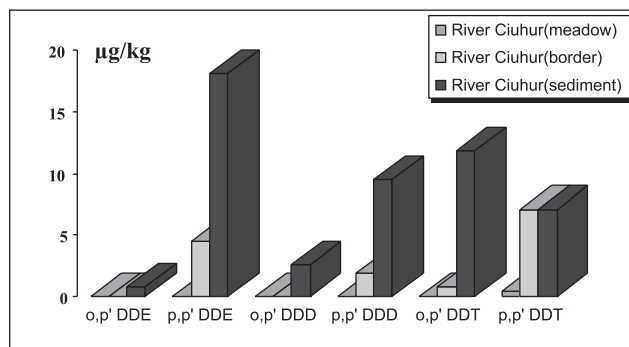


Figure 6. DDX compounds in soil (20--40 cm) and aquatic sediment r. Ciuhur, Republic of Moldova

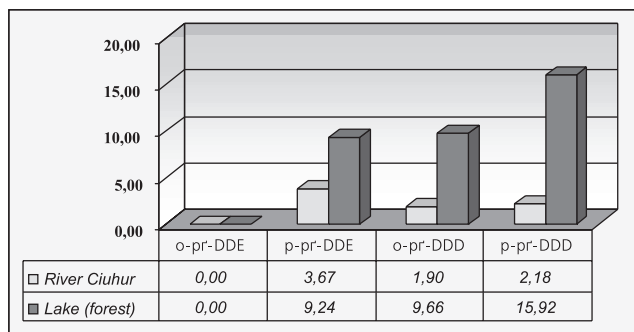


Figure 7. DDX compounds in aquatic sediments (River Ciuhur, Lake (forest))

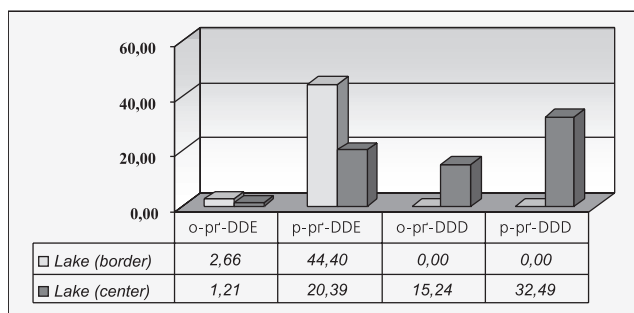


Figure 8. DDX compounds in aquatic sediments (Lake Colonita), Republic of Moldova

Analyses

After clean-up, the extract was concentrated in 100 µl and analyzed GC using a non-polar capillary column. A Finnigan Ion Trap Spectrometer ITS – 40 was used as detector. The limit of quantity was 2,0 µg/kg d.m for PAHs and 0,5 µg/kg d.m for DDX compounds.

RESULTS AND DISCUSSION

The total concentrations of $\Sigma 16$ PAHs are small. The results differ much depending on the sediment type (river/lake) and place of sediment (border/center of the lake) (Figures 1 and 2). The sum of sediment PAHs is in a range of 428,88 µg/kg d.m. (river Ciuhur), 59,64 µg/kg d.m. (center of the lake Colonita), 17,05 µg/kg d.m. (border of the lake Colonita) and 50,4 µg/kg d.m. (lake placed in the forest ecosystem, comparatively far from agricultural fields), takes in our experiment as a witness. The highest amount shows pyrene (65,2 µg/kg d.m., river), fluoranthene (15,8 µg/kg d.m., lake (center) and 10,5 µg/kg d.m. of fluoranthene in the sediments collected from the lake (forest) (Figures 1, 2, 3 and 4).

Concentration of Σ DDX shows high concentration and geoaccumulation, in soil (meadow), border of the river and aquatic sediments (Figure 5 and 6). p, p' - DDE is the dominant metabolite in soil and sediment samples and shows together with p, p' - DDD high amount in sediments collected from the lakes (Figures 7 and 8).

Although the use of organochlorine pesticides ceased in the Republic of Moldova in 1970, the results indicate that even after a period of 30 years, residues still persist in soils (meadow) and are geoaccumulated in the aquatic sediments.

CONCLUSION

Although the use of organochlorine pesticides ceased in the Republic of Moldova in 1970, the results indicate that even after a period of 30 years, residues still persist in soils (meadow) and are geoaccumulated in the aquatic sediments. The destruction of the surface sediment by navigation traffic and excavation activities may have serious consequences for the underlying groundwater aquifers. Although pollutants are transported by water systems, sediments reflect the physicochemical and ecological status of the waters. Sediments act as natural buffer and filtration systems in the terrestrial - limnological cycle in particular. The sorption, enrichment or degradation of persistent

organic pollutants, however, is not unlimited. The investigated aquatic sediments represent an integration of the contaminants emitted over time and may be used an indicator of local and short - term inputs.

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PESTICIDE POLLUTION IN BENTHIC ORGANISMS AND SEDIMENT OF SOME RIVERS AND LAKES IN NORTHERN ITALY

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ABSTRACT

Sediments act as a reservoir for organic persistent chemicals. The analyses of micro-pollutant concentrations both in sediments and in benthic invertebrates give important assessment endpoints for the evaluation of ecological risks in aquatic environments, particularly when persistent organic contaminants are taken into account.

In the present study the main organic micro-pollutants (POPs) were analysed in sediments of rivers and lakes of Northern Italy. When present, also benthic oligochaetes were sampled and analysed. In one case POPs concentrations were also measured in soil and earthworms along a riverbank.

Micro-pollutant concentrations in sediments ranged from 2.1 to 623.0 ng g⁻¹ d.w. for DDT, from 0.1 to 111.1 ng g⁻¹ d.w. for HCH, from 0.1 to 16.4 ng g⁻¹ d.w. for HCB and from 10.1 to 3053.8 ng g⁻¹ d.w. for PCB.

In general, rivers were more contaminated than lakes, especially in areas close to their mouth. One of the most contaminated sites was found in the Lambro river close to Milan, one of the most industrialised and densely populated areas of Northern Italy. POPs concentrations in worms were comparable with those found in sediments in most cases.

Data provided by the present study could be useful for the identification of the sources of persistent organic pollutants in Northern Italy in order to promote the restoration and to guarantee the protection of the aquatic environments.

Keywords: organic micro-pollutants, sediment, oligochaetes

INTRODUCTION

Organic micro-pollutants are known for their high persistence and lipophilicity. Due to these properties, organochlorine pesticides present a very low solubility in water, showing a high affinity for sediments and for fatty tissues of animal bodies where they can be easily accumulated. Concentrations in sediments and in organisms depend both on the physico-chemical properties of these substrates and on the partition coefficients (K_{ow}) of the different xenobiotics, which can strongly modulate the bioavailability of micro-pollutants. As a result, the toxicity due to the exposure of benthic organisms to contaminated sediments is variable and this could explain the uncertainty of linking a biological effect to a pollutant concentration. From the analysis of both sediments and organisms, an idea of the localisation of "hot spot" pollution areas and of the impact of organic micro-pollutants on the environment can be achieved. This information can be important for the evaluation of the ecological risks and can be of help in the restoration of the aquatic environments.

Northern Italy is the most industrialized area of the country and agriculture is well developed on a wide scale, too. Even if the amount of the used pesticides in Italy has reduced by 25% in the last ten years, the national consumption is still around 110,000 t y⁻¹ (Agrofarma 2000).

The majority of the used pesticides belong to fungicides but even insecticides and herbicides are used in large quantities. The reduction of the pesticide use may be caused by the new technologies, which foresee the limitation of their uses and to the development of other new strategies to prevent damages to cultivation. Moreover, during the last years various legal regulations considering the environmental protection have been issued and among them the regulation of pesticides plays an important role. The Italian legislation on production, trading and use of pesticides started with the first law in the 1960ies (D.L. 30.4.1962, n. 283), but the most significant regulation (D.L. 17.03.1995, n. 194) comes from the European directive 91/414/CEE. Currently in Italy 443 compounds are certified and a more and more careful control of these products before their trading exists: this will lead to the withdrawal of about 100 of these compounds in the next five years (Auteri ICPS, pers. comm.). Still this is not enough to solve the contamination of the environment, but it represents the first steps towards the recovery of the environment.

The present study deals with an evaluation of the levels of contamination of the main organic micro-pollutants (PCB, DDT, HCH and HCB), representatives of both industrial and agricultural contamination in sediments and in benthic worms collected in some riverine and lacustrine environments of Northern Italy.

MATERIALS AND METHODS

Sediments were collected both in rivers and in lakes in Northern Italy, as reported in Table 1 and Figure 1 during three different periods (April 2001, June 2001 and June 2002). Bottom river sediments were sampled with a steel spade from the top 5-7 cm layer of sediment in depositional areas along the banks. Lake sediment were sampled with a dredge at the deepest point, with the exception of those of Lake Maggiore which were sampled in the area of the inlet of the River Toce.

Oligochaetes worms were also sampled and then analysed in June and July 2001 at Milan (River Lambro) and in June and September 2002 at Zibido (River Lambro Meridionale). On this last occasion soil and earthworms were also collected in the soil surrounding the bank and analysed.

After collection, sediments were wet-sieved at 250 µm to remove indigenous fauna (Day et al. 1995). A small amount (about 3 g w.w.) of sediment and of oligochaetes was freeze-dried and then extracted for 12 and 8 h respectively in a Soxhlet apparatus using a mixture (1:1) of n-hexane and acetone (100 ml). The extracts were concentrated to 2 ml by rotary evaporator and then digested with 3 ml of H₂SO₄ for 24 h to remove all the organic matter. The digested samples were then concentrated (2 ml) and cleaned on columns (silica Florisil SIGMA) with a thin top layer of Na₂SO₄ to catch residual water. In the case of sediments, copper was added to retain sulphur compounds; before use it was left in HCl (18%) rinsed after 24 h with dechlorinated water until pH 7 was reached, then with ace-

tone and hexane. The column was eluted with 25 ml of hexane and the purified extract was concentrated to 2 ml. Samples (1 µl) were injected into a ThermoFinnigan Gas Chromatograph equipped with a 63Ni electron capture detector (ECD). The on-column system was used for injection. A fused silica capillary column (HP-5 Crosslinked 5% PH ME Siloxane, 60 m x 0.25 mm i.d.) with a film thickness of 0.25 µm was used. After one minute at 100°C, the temperature programme runs to 180°C at 20°C min⁻¹, then from 180°C to 200°C at 1.5°C min⁻¹, from 200°C to 270°C at 3°C min⁻¹ and at the end it remains at 270°C for 20 min. The carrier gas was helium at 1 ml min⁻¹ and the auxiliary gas was nitrogen at 40 ml min⁻¹. The detector temperature was fixed at 280°C. Analysis was performed for PCB, DDx, HCH and HCB. Known quantities of 23 PCB congeners of Aroclor 1260 (Alltech) were used as reference standard for PCB; a prepared standard mixture of pure DDT homologues, HCH and HCB was used as reference standard for their determination.

The external standard method was used for quantification. Peaks were automatically integrated using the ChromCard 1.16 software (ThermoFinnigan). Analyses were performed in duplicate; the detection limits were 0.1 ng g⁻¹ for PCBs and 0.05 ng g⁻¹ for DDx, HCH and HCB.

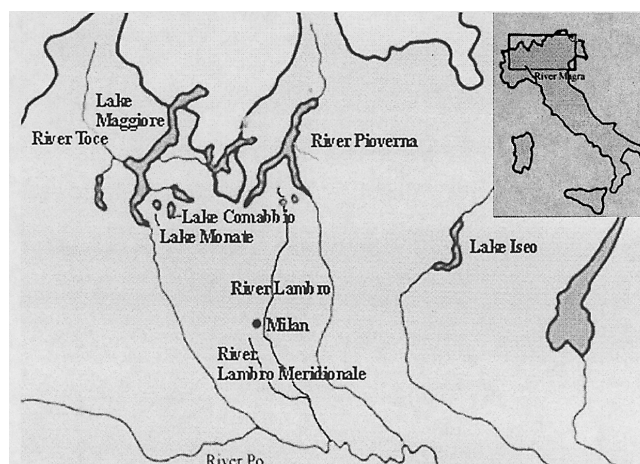


Figure 1: Map of Northern Italy with the sampled sites

Lakes	Rivers
Maggiore (April 2001)	Toce (April 2001)
Monate (April 2001)	Magra (April 2001)
Comabbio (April 2001)	Pioverna (April 2001)
Iseo (April 2001)	Lambro (June 2001)*
	Lambro Meridionale** (June 2002)

* sampled in seven sites along the banks

** sampled in two sites along the banks

Table 1: Sites and period of sampling (in brackets).

Sediment samples	Total Sum DDx (ng g ⁻¹ d.w.)	Total Sum PCB (ng g ⁻¹ d.w.)	Total Sum HCH (ng g ⁻¹ d.w.)	HCB (ng g ⁻¹ d.w.)
Maggiore	70.1	45.9	7.7	0.9
Monate	8.7	30.6	0.9	0.3
Comabbio	18.5	86.3	0.1	3.6
Iseo	2.6	14.8	n.d.	0.3

Table 2: Concentrations of the main organic micro-pollutants in sediments collected in different lakes in Northern Italy. The coloured square underlines the maximum values measured.

Sediment samples		Total Sum DDx (ng g ⁻¹ d.w.)	Total Sum PCB (ng g ⁻¹ d.w.)	Total Sum HCH (ng g ⁻¹ d.w.)	HCB (ng g ⁻¹ d.w.)
Toce		115.7	92.8	17.7	9.5
Magra		3.4	58.2	0.1	0.1
Pioverna		2.1	37.6	1.6	n.d.
Lambro	Merone	2.1	10.1	0.5	0.2
	Lambrugo	3.5	21.9	0.7	1.3
	Agliate	1.5	16.1	1.2	n.d.
	Parco Monza	2.9	39.5	1.2	0.5
	Milan	167.0	3053.8	1.6	16.4
	Salerano	35.7	563.0	18.4	6.3
	Lambrinia	21.2	255.7	27.6	10.8
Lambro Meridionale	Zibido	19.5	104.0	23.3	0.3
	Villanterio	623.0	1840.3	111.1	10.2

n.d. = not detectable

Table 3: Concentrations of the main organic micro-pollutants in sediments collected in different rivers in Northern Italy. For River Lambro and River Lambro Meridionale the concentrations measured in different sites along the banks are reported. The coloured square underlines the maximum values measured.

RESULTS AND DISCUSSION

The levels of the main organic micro-pollutants in sediments are reported in tables 2 and 3. On the whole, concentrations of organic micro-pollutants were higher in river sediments than in lakes.

Among lakes a significantly higher concentration of DDT was found in Lake Maggiore sediments. This is not surprising because the use of DDT, not its production, is forbidden in Italy and this pesticide has been discharged until 1996 by a manufacturer into the lake through its main inlet, the River Toce (Ceschi *et al.* 1996). For this reason also the River Toce sediments present a huge amount of DDT, exceeded only by the highest DDT value found at one site of the River Lambro Meridionale (Table 3). The concentrations of total sum DDx of Lake Maggiore sediments are comparable with those found recently (CIPAI 2002) and in 1996 (Guzzella *et al.* 1998) in sediments collected in an area close to our sampling site. These concentrations are likely to increase in the near future since total sum DDx found in the sediments of River Toce were particularly high due to floods that occurred before our sampling campaign. This would mean that the ground surrounding the river is still heavily polluted and as a consequence both the river and the lake cannot be considered safe from the contamination. Moreover PCB concentrations in sediments of River Toce and in Lake Maggiore sediments are noticeable higher compared to the previous sediment analyses (Guzzella *et al.* 1998; CIPAI 1999).

The concentration of PCB was found to be significant in sediments from the River Lambro at Milan; this high value shows the great impact of the city on the river since up to now the urban discharges of the city were untreated and flowed directly into the river. A first line of one of the three planned treatment plants of the city of Milan has started to operate only on April 2003 and it will take another two to five years to complete this system.

High concentrations of HCHs were found in the southern part of both River Lambro and River Lambro Meridionale, probably because of the highly developed agriculture in the area where the rivers flow. HCHs, especially lindane (gamma-HCH), are still used in mixture, notwithstanding their restriction by law.

In general, apart from the highest PCB and DDT values, the concentrations found in rivers and lakes of Northern Italy are within the range of, or even lower than, the levels observed in other Italian and European environments (Hernandez *et al.* 1992, Provini *et al.* 1995 Chevreuril *et al.* 1998, De Cooman *et al.* 1998, Fernandez *et al.* 2000, Kocan *et al.* 2001, Camusso *et al.* 2002).

Since the levels in sediments are not informative on the bioavailability of these compounds, the POP concentrations in benthic organisms have to be determined in order to obtain important information for the evaluation of ecological risks in the aquatic environments. Our findings show that the worms were always very contaminated but each pesticide accumulates without a specific trend.

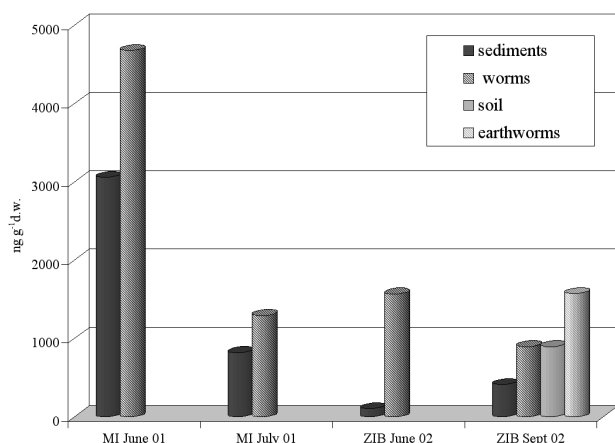


Figure 2: PCB concentrations ($\text{ng g}^{-1} \text{d.w.}$) in sediments and worms measured at Milan (MI) and Zibido (ZIB) in summer 2001 and 2002. PCB concentrations in soil and earthworms measured at Zibido in September 2002 are also reported.

The concentrations of the micro-pollutants in worms sampled in the sediments of the River Lambro and of the River Lambro Meridionale were 0.5-2.2 times higher, compared to sediments, with the only exception of oligochaetes collected at Zibido in June 2002 when the BCFs were noticeable higher. In general, PCB (Figure 2) were accumulated more than DDX and HCH (Figure 3) and this could depend on the different lipophilicity of these pesticides. Moreover, it can be observed that the different PCB bioaccumulate in different ways depending probably on their molecular size.

An example of this behaviour is reported in Figure 4: worms bioaccumulate the PCB congeners, which present a low number of chlorine atoms (those on the left side of the figure), more than the other ones, notwithstanding their presence in the sediments.

Apparently no reasons can be found to explain the highest degree of bioaccumulation of worms collected at

Zibido in June 2002; perhaps the observed differences could be ascribed to the changeable flow conditions of the rivers and to the weather preceding the samplings. Even the soil and the earthworms collected along the shores of the River Lambro Meridionale present a contamination by micro-pollutants, particularly PCB and HCH. The observed

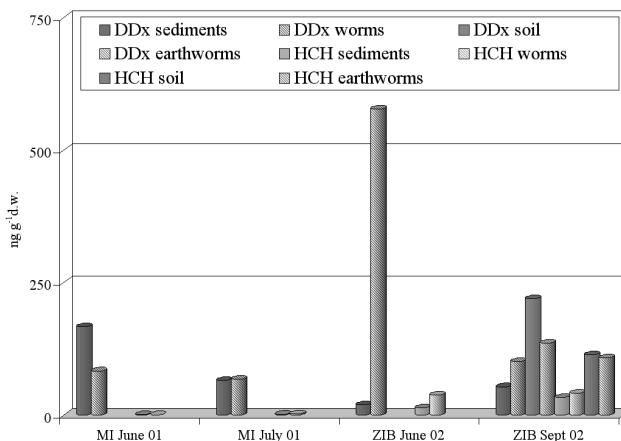


Figure 3: DDX and HCH concentrations ($\text{ng g}^{-1} \text{d.w.}$) in sediments and worms measured at Milan (MI) and Zibido (ZIB) in summer 2001 and 2002. DDX and HCH concentrations in soil and earthworms measured at Zibido in September 2001 are also reported.

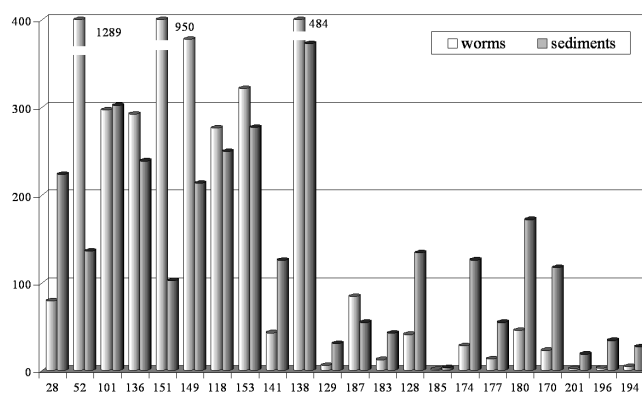


Figure 4: Concentrations of the different PCB congeners ($\text{ng g}^{-1} \text{d.w.}$) in sediment and worms collected at Milan in June 2001.

values of pollutants mean that the contamination of the river is not restricted to its water and sediment but is directly transferred in the surroundings. This could be the reason why PCB, which is an indicator of industrial contamination, is also present in terrestrial organisms living in this agricultural area and we can suppose that the contamination spread out, reaching also the terrestrial trophic chains.

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ECOTOXICOLOGICAL RISK ASSESSMENT OF OBSOLETE PESTICIDES

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Ecological situation in Ukraine causes concern because of chemical substances (pesticides) accumulation. The accumulation of obsolete pesticides started before the USSR's collapse.

unfitted for usage, represent the second source of accumulation. In this case, the term of un regulative stock itself becomes a danger and results in formulation of disintegration products and appearance of mix products.

OBP are dangerous for population and biota, because during the long period of storage toxic substances are created as result of natural factors action and chemical interaction, (phosphate, phosgene, dibensofuran, methyl Mercury, oxide of nitrogen etc.) and they can migrate into contacting media (water, soil, air).

What are the approaches to the risk assessment of these substances for environment and public health? Determination of the risk, namely, the evaluation of unde-

Initial compounds	Evaluative factors	Type of reaction	Products of transformation	Character of toxicological action
Derivatives of phosphorous and di-thiophosphorus acids	Insulation, moisture, oxygen	Hydrolysis, oxidation	Phosphates, dithiophosphates	Systematic, toxicological
Chlorinated cyclic and polycyclic compounds (GCCG, DDT, polychlorcamphene)	Fire, interaction with nitrogen soils	Pyrolysis, Synthesis	Phosgene, chlorcyanes, chlorinated dibenzodioxins, dibenzofurans	Systematic, , neuro-toxic, actions
Derivatives of chlorophenoxyalkyl-carbonic acids	Illumination, moisture	Hydrolysis	2, 4-Д, chlorophenoles	Common-toxic, neuro-toxic action
Mercury compounds	Natural processes in soils and water	Decomposition, Synthesis	Methyl mercury	Neuro-toxic

Table 1. Examples of toxic pesticides transformation

It is generally known, that the high toxicity causes a strongly expressed remote effects on warm-blooded organisms and affects the stability of environment, that is why toxic substances were prohibited. Thus the way of obsolete pesticides accumulation determines the appearance of not only simply dangerous but even highly or extremely dangerous situation. The pesticides, which became obsolete because of the incorrect transportation, or pesticides stocks,

sirable events danger, which can appear at a certain place, as well as prognosis of probable damages are the most correspondent to the task of the risk assessment. Specificity of the risk assessment comprises firstly calculation of the separate pesticides risk, secondly, calculation of the numerous stocked pesticides as a source of toxic wastes and thirdly consideration of the certain ecological and toxicological conditions.

Toxicological – hygienic characteristic of obsolete pesticides				
Physical-chemical parameters		Toxicometry		Hygienic standards
Estimation of combined effects				
Volume (mass) of pesticides in storage	Temporality and mode of contact	Natural conditions		
		Ultra-violet radiation	Development of microorganisms	Acidity of surrounding
Estimation of ecological and toxicological conditions of pesticides storage includes the following steps:				
State of the storage territory		Landscape features for toxins spreading	Probable consequences for animals and plants	Temporality of ecological – toxicological situation
Sanitarian and technical conditions	Distance from dwelling			
Analysis and prognosis of unfavorable effects action and technological aspects of ecological catastrophe avoidance				

Table 2. Risk assessment of obsolete pesticides

Thus, the risk assessment is a complex and multi-staged process. The risk assessment of separate pesticides must be provided by the usage of toxicity parameters on the basis of WHO classification accepted in Ukraine. It should be noticed that calculation of the index migration from soil to neighboring media is essential addition to mentioned classification.

Repackaging of pesticides temporary in bigger storages in containers, which is widely recommended now, is not a radical way to solve the problem because it will promote deterioration of ecological situation, extension of the problem solution for decades and additionally is rather expensive one.

MIGRATION OF SIMAZINE WITH EROSION PRODUCTS DURING SNOW MELT

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ABSTRACT

The effect of the cultivation type of the eroded gray forest soil (i.e., with or without turnover of a furrow slice) on the specific features of simazine migration with snow melt and washed soil was investigated during the period of spring snow melting. The main factors affecting toxicant transformation in the soil and its removal with erosion products under the conditions of agro-landscape with slopes of up to 30 were analyzed in detail.

INTRODUCTION

Environmental control of different pollution categories gains an increasing concern every year. The processes of entering, transmission and transformation of toxicants proceed under the influence of various factors. Based on the spatial or temporal interactions among these toxicants, the local, regional and global prognosis models of a state of natural environment were designed (Borzilov & Drogolubova, 1989; Lunev, 1989; Ostromogilskiy *et al.*, 1989; Ahuja, 1986; Eduljee, 1987). Nevertheless this problem remains crucial and acute especially for environmental management where urban, agricultural land as well as reservoirs (rivers, lakes, water reservoir etc.) are suffering and affecting by the greatest load of xenobiotics.

The major available experimental information in the literature reveals that there are two basic means through which toxicants enter into the environment during agricultural practices. The first mean is through technological applications of such chemicals to soil and plant crops according to agricultural requirements. Second mean is through migration of pesticides and their metabolites with the surface run off (solid or liquid), which increased with snow melting or rainstorms.

Obviously thermo destruction is the most ecologically and economically effective method for obsolete pesticide's destruction.

The problem of the risk assessment is deep and not limited by existing approaches. Value of the risk varies very strongly and depends not only on physical-chemical and toxicological properties but also on regional natural-geographical and social-economics features. Therefore there is a necessity to develop a complex approaches, which will take into account the system analysis of many factors.

Bobovnikova *et al.* 1979, 1983 have shown that migration of DDT in a solid phase surface run off formed on eroded fields the recorded 1000 folds higher concentration compared to its concentration in the aqueous phase. Moreover, results revealed that the period of the spring high water was accounted for up to 70% of pesticides flow, a value correlated with the water run off. Baly & Nikolson, 1979 and Bobovnikova *et al.*, 1979 studied the run off coefficients of some persistent and chlororganic pesticides on various types of natural catchments during the period of spring high water. Nevertheless, the necessity of analytical accuracy and precision in the determination of the existing ecotoxicological situation and the prognosis of its subsequent modifications represented a must.

The aim of the present work was to evaluate the influence of some types of the basic soil tillage (with and without turnover of a furrow slice) on the pattern of simazine migration with a surface run off of thawed water and soil washed off.

MATERIALS AND METHODS

To evaluate the removal pattern of pesticides with erosion products, field observations were taken. These observations were recorded under stationary conditions of soil-erosion. The investigated sites were located on the slope of the south-east ex-position of the small river Lubozhikha catchment, the right tributary of Oka River (South of Moscow region).

Soil cover of selected experimental plot was represented by weakly eroded Gray Forest soil. Humus content in plowing horizon was 2.0-2.3%. The sum of absorbed bases was 12.5-18.9 mg-equivalent/100 g of soil. Water pH ranged between 6.5 and 6.8. Humus horizon on granulometric composition represented by heavy clay loam in which volumetric mass from 1.15 to 1.30 g/cm³. For these types of soils, the average provision of the mobile forms of nitrogen, phosphorus, and potassium is characteristic and they are in constant intensive agricultural use.

The investigations of erosion-hydrological processes were carried out on water-balance runoff plots 100 m × 18 m in size, which placed in by the watershed part of a slope. The steepness of slope changes from 0030' to 3030' downward. The field study tool place for five-course rotation. Thus two kinds of principal soil cultivation – plowing to 20-22 cm depth and subsurface tillage to the same depth were carried out annually during autumn in every field. Generally, standard

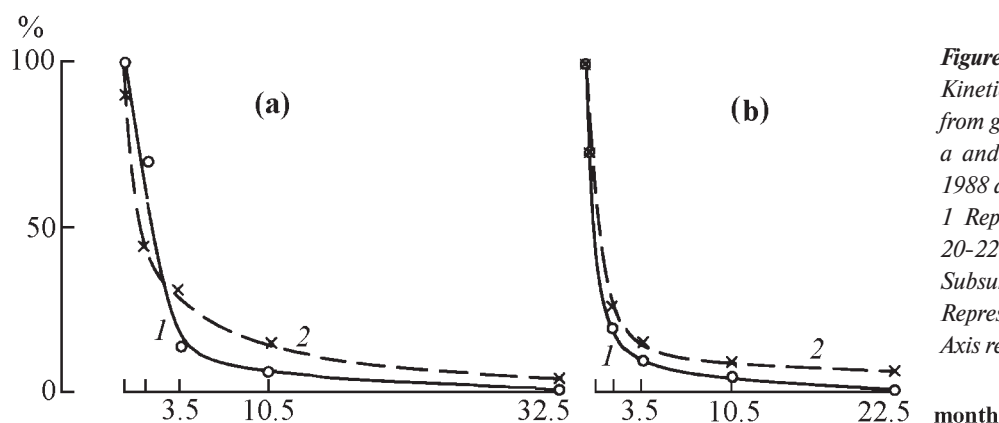


Figure 1:
Kinetics of Simazine Disappearance from gray forest soil:
a and b Represents Applications at 1988 and 1991 Respectively.
1 Represents Soil plowed Down to 20-22 cm Depth and 2 is Represents Subsurface Tillage. The X-Axis of Represents Time in months while Y-Axis represents Simazine content, %.

methods were used for soil erosion investigations (Surmach *et al.*, 1975; Bogolyubova *et al.*, 1975; Dospekhov, 1979).

During the experiment, the tractor sprayer at the rate of 1.6 kg/ha applied 80%-moistened powder of simazine in one day prior to sowing of fodder maize in 1988 and repeatedly in 1991 (rate of solution flux was 250-300 l/ha).

The dynamics of simazine content in soil was estimated by sampling and analysis of samples in 0-5 and 5-10 cm layers within 24-hours and 1.5; 3.5; 10.5; 22.5 and 32.5 month.

The content of simazine in soil, thawed water and washed off soil were determined using gas chromatography (Methods of definition, 1977).

RESULTS AND DISCUSSION

The analysis of the results of the transformation of toxics in soil of slope grounds either obtained during the present work or from previous researches revealed that it is necessary, alongside with processes of disappearance, to take into account the possible removal of the pesticides with the products of erosion.

The kinetics of the simazine disappearance applied on a surface of gray forest soil before sowing of maize; on both variants of the basic soil tillage (with and without turnover of a furrow slice) revealed identical characters and are featured by a hyperbola of the first order with two nonequivalent periods (Figure 1).

In first period (during vegetation), the very high disappearance rate of simazine from the upper surface (10-centimeter) soil layers with coefficient $k_1=2.0$ was observed. Its concentration decreased as a result of microbiological degradation, translocation by plants, photolysis on the soil surface etc. At the end of this period, soil with plowing contained 9.0-13.6% while subsurface tillage contained 12.6-29.3% of the simazine applied that exceeds the level of Extreme Allowable Concentration (EAC) by 3-8 folds.

In the second period, the disappearance rate of simazine exhibited sharp retardation ($k_2=0.2$). As a result, level of soil pollution tillage by subsurface tiller reached extreme allowable values only through 22.5 - 32.5 months after application. At the same time, removal of toxicants with erosion products can occur.

The analysis of data obtained during the field experiment showed that the type of the basic soil cultivation can render

the essential influence on simazine distribution in the top layer of soil. So after 3.5 months (end of the first vegetation season), 68% of toxicant was in the 5-10 cm layer on the variant with plowing while on subsurface tillage its concentration recorded 64 % focused in the top 5 centimeter horizon. These singularities of the herbicide distribution in the top layer of soil have defining value at its removal with erosion products for the catchment limits. During thawing, snow of the upper layer of soil subjected to a gradual thawing which provides soil with a condition of total moisture capacity and fluid consistence. The washed off soil decreased during the process of its top layer thawing.

It is established that in the period of spring high water the sorbed residues of simazine together with eroded soil are removed from boundary of agro landscape even under the conditions of slopes with steepness up to 30. However before snow melting, such climatic and erosion-hydrological conditions could take place when the formation of a run off on slopes does not take place, and all thawed water seepages into soil. During the present study, such conditions occurred during 1989 and 1990 (Demidov *et al.*, 1993) and only during March 1991 the formation of water run off associated by soil wash off were marked. It is necessary to note that at the primary application of simazine during 1988 (1.6 kg/ha) its content (through 32.5 month) in the top layer of soil (0-5 cm), plowed by subsurface tiller recorded 0.55 mg/kg, and on plowing during the same time it was not detected at all (Table 1). During snowing (before melting) and water thawing (in the period of snow melting), traces of the herbicide were detected on both variants of the basic plow of soil. At the same time in a solid phase of the soil plowed by subsurface tiller, its content reached 1.37 mg/kg.

At the secondary application of simazine during May, 1991 and with the same dose at the end of March, 1992, the content of the herbicide in top layer of the soil on the variant with subsurface tillage reached 0.58 mg/kg and in the thawed water recorded 0.00004 mg/l while in the washed off soil recorded 1.25 mg/kg. In the spring of 1993, no simazine was detected in the thawed water and its content in top layer of soil (0-5 cm) recorded 0.11 mg/kg while in the washed off soil it reached 0.31 mg/kg. It is necessary to note, that the presence of simazine in the top layer of soil and solid run off formed on plowing was not detected.

During the present study, there were different conditions where thawed water run off was formed which results in soil washing off. Volume of the water run off during the period 1991-1993 changed from 0 to 25 mm (Table 2). Thus the amount of soil washed off changed from 0 on the variant with plowing (1991) to 2.20 ton/ha on subsurface tillage variant (1993). The simazine removal depends on the amount of soil losses and the contents of the herbicide in the soil before snow melting. Accordingly, its removal changed from 310 to 682 mg/ha. It is necessary to note the positive effect of using plowing to 20-22 cm depth in comparison with subsurface tillage to the same depth, in all the observations years. This was expressed by the lack of toxicant removal with thawed water and washed off soil.

Thus, results of the present study revealed that, during the evaluation of the processes of transformation and transmission of pesticides on slope grounds, alongside with other factors, it is necessary to take into account and type of the basic plow of soil.

CONCLUSIONS

The application on slope grounds various. Erosion-preventives of soil plows and application of pesticides to fight the green weeds, illnesses and depredators of plants frequently results in environmental contamination. Results of the present study showed that using of subsurface tillage of soil at 20 -22 centimeters depth in comparison with plowing to 20-22 cm depth creates conditions of concentration of the basic amount of the applied simazine in the upper 5-centimetric soil layer. During snow melting, the upper soil layer first is washed off, that results in the removal of the herbicide with fine earth on which it is adsorbed. It is also shown that even after 2-3 years of the application, removal of simazine with washed off soil were observed. In the same time, by using plowing at 20-22 centimeters depth, no pesticide was detected in top soil layer or in and the washed off soil.

Time (Year, month)	Pesticide Concentration (mg/kg)	
	Plowing to 20-22 cm	Subsurface tillage to 20-22 cm
1988		
After application	18.82	16.78
1.5	13.44	4.63
3.5	2.56	3.16
1989		
10.5	1.87	2.81
1991		
32.5	0/0*	0.55/1.37*
After application	13.89	13.89
1.5	2.86	2.91
3.5	1.25	1.75
1992		
10.5	0/0*	0.58/1.25*
1993		
22.5	0/0*	0.11/0.31*
EAC (sanitary), mg/kg	0.5	0.5
EAC (phytotoxicity), mg/kg	0.1	0.1

* In numerator the given contents of simazine in the upper (0-5 cm) of the soil layer, in denominator, its content in the washed off soil; EAC is extreme allowable concentration

Table 1: Residue Levels of Simazine in Soil Surface Layers (0-10 cm) and in Solid Run off Based on the Method of Basic Soil Plowing.

Observation Years	C** (mm)	σ	W (t/ha)	Content in		Removal, mg		
				Water (mg/l)	Fine earth (mg/kg)	With water	With soil	Sum
1991	0	0	0	0	0	0	0	0
	5.5	0.16	0.25	0	1.37	0	342.5	0342.5
1992	23.1	0.40	0.51	0	0	0	0	0
	25.0	0.39	0.24	4 10 ⁻⁵	1.25	10.0	300.0	310.0
1993	16.8	0.56	2.00	0	0	0	0	0
	17.7	0.48	2.20	0	0.31	0	68.0	682.0

**C is the layer of thawed water run off; σ is the coefficient of water run off; W is the soil loss; in numerator data received on variant with plowing to 20-22 cm depth, in denominator with subsurface tillage to 20 -22 cm depth.

Table 2: Influence of the Basic Plow Types of the Grey Forest Soil on Simazine Removal with Erosion Products

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DIFLUOROMETHYLATION OF HYDROXY-CONTAINING PESTICIDES, A NEW METHOD OF ANALYSIS AND UTILIZATION

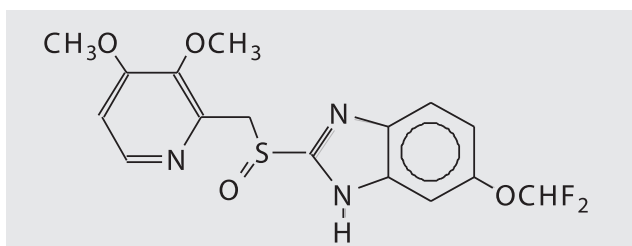
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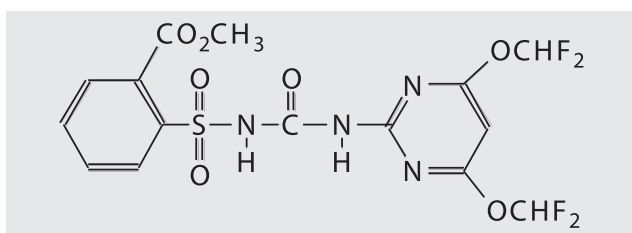
The chemistry of fluorine-containing compounds has been tremendously developing owing to their unique properties, such as high thermal stability and lipophilicity. Fluoroorganic compounds have been frequently referred to bio-related materials, medicines and agrochemicals. Many fluorine-containing compounds exhibit significant agricultural importance, for example, insects' growth regulation.

A considerable activity in joining new fluorine containing groups can be seen in the recently developed pesticides. Most pharmaceuticals contain mainly fluoro- or trifluoromethyl- groups. New chemicals, such as: Pantaprazole (new antiulcer drug), which contains a difluoromethoxy group; Flucythrinate (insecticide, Du Pont); and Primisulfuron Methyl or Beacon (herbicide, Ciba-Gaigy), which contains a difluoromethoxy group too [1], have appeared very recently.

Pantaprazole

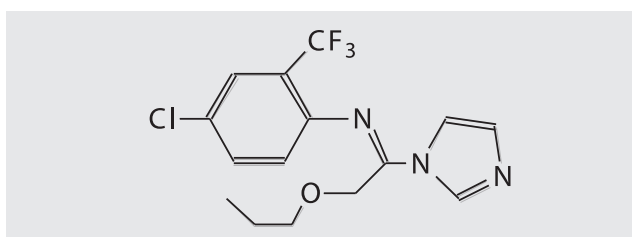


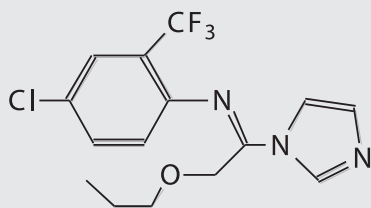
Beacon



Fluorinated pesticides are present in all pesticide categories and most chemical classes, such as (Bayer) Euparene and (Nippon Soda) Trifmine

Bay 47531 (Bayer) Euparene

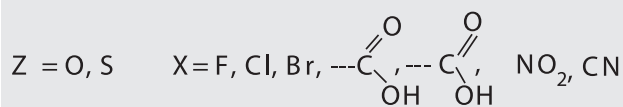
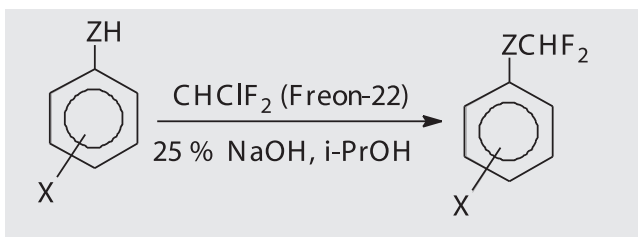


NF-144 (Nippon Soda) Trifmine

Rodenticides and plant growth regulators have a number of highly active fluorinated molecules [2]. The methods of introducing a fluorine functional group to an organic compound have been widely investigated. Freon-22 is supported to be a good starting material to introduce a fluorine functional group to organic compounds.

The difluoromethoxy group, OCHF_2 , often contributes special biological properties to organic molecules. Apart from its high lipophilicity exceeding other groups, such as $-\text{OCH}_3$ or $-\text{NO}_2$, OCHF_2 , it is able to act as a hydrogen donor through hydrogen bonding and actively enhances biological activities. Difluoromethoxy group incorporated into amino acids is used in sugar chemistry, and plays an important role in the sphere of herbicides production and liquid crystals [3].

The present work attests the possibility of convenient modification of some important types of aromatic compounds, such as phenols and thiophenols, into fluoro-containing moieties, which can be shown on example of compounds model – derivatives of phenols, containing various atoms and functional groups e.g. bromine-, fluorine-, chlorine-, carboxylic-, carbonyl-, cyano- and nitro- groups:



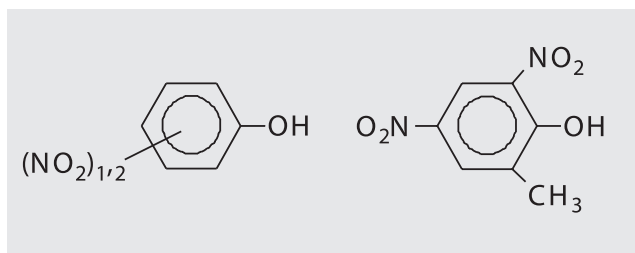
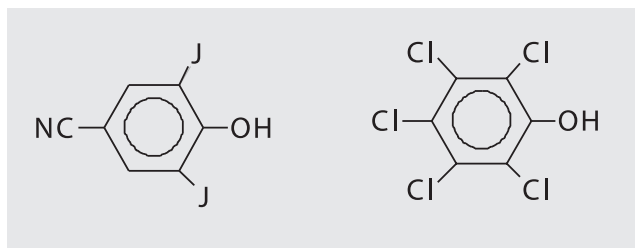
During the present work simple and technological methods were developed to prepare the aryldifluoromethoxy and aryldifluoromethylthio ethers with various substituents in aromatic ring [4]. All compounds obtained are low toxic, stable products, easily detected and identified by GLC.

The reaction proceeds via the formation of difluorocarbene in the presence of strong bases, namely sodium hydroxide or sodium ethylate. In last case, the method is fulfilled by means of reaction performance under conditions of interphase transfer (K_2CO_3 – abs. ethanol). This method is particularly important in the difluoromethylation process of water labile phenols.

This is the first time, when we are able to demonstrate the possibility of difluoromethylation of aliphatic, aromatic and heterocyclic aldehyde and ketone oxides with the formation of new types of compounds, containing difluoromethoxy group near the nitrogen atom.



These reactions can be used for the utilization of difficult obsolete pesticides such as:

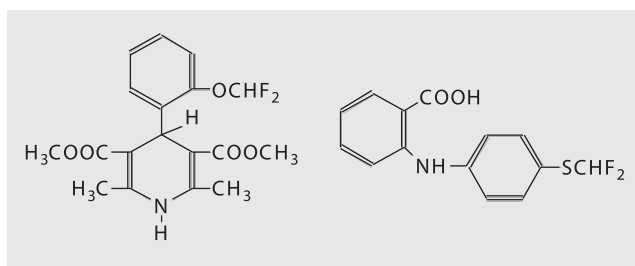
**Nitrafen****Dinitroortocresol****Ioxynil****Pentachlorophenolate Sodium**

nitrafen, dinitroortocresol, Ioxynil, Pentachlorophenolate Sodium and other hydroxy-containing pesticides.

The use of Freon-22 for the modification of the hydroxy-containing compounds is interesting from both sides: from the point of technical pesticides utilization and decrease of Freon influence on the environment.

On the base of the present study results the method of difluoromethylation of some substituted phenols such as salicylaldehyde (2-hydroxybenzaldehyde) and 4-nitrothiophenole has been developed and applied in industry.

Based on the above-mentioned difluoromethoxy containing intermediates, new medical preparations have been developed and nowadays they are produced by Ukrainian chemical and pharmaceutical industry:

**Foridon****Difloran**

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DETERMINATION OF SOILS CONTAMINATED WITH ORGANOCHLORINE PESTICIDES

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Ukraine is a country with highly developed agrarian production sector. The production of agricultural products requires the use of mineral fertilizers, chemical agents for the protection of plants from pests, vermin and weeds, specialized crop rotation, different methods of soil processing, lands melioration, etc. Statistically, a huge amount of pesticides result from agricultural production, as 70.2% (42 million hectares) of Ukraine (60.4 million hectare) is agricultural lands. Of this area, 34.3 million hectares (81%) are arable land [1].

Almost in every collective farm on the Ukrainian territory there was a storehouse where large amounts of pesticides were stored during years including persistent organochlorinated pesticides. A sanitary zone was located around each storehouse; its area depended on the amount of pesticides stored in the storehouse. During many years, pesticides were repacked, reloaded and prepared near these storehouses. As a result of long-term and uncontrolled exploitation of pesticide-contained storehouses, but also at former airfields of agricultural aviation, soil pollution with persistent pesticides has occurred at such zones. Levels of such pollutants highly exceed the maximal acceptable limits for soils.

These soils are considered as a source of pollution with persistent toxic organic compounds to the neighbouring territories and groundwater as a result of air and water transportation, migration of soils and migratory species.

During the last years, prohibited pesticides were removed from these storehouses and currently are stored in centralized storehouses. Accordingly, more than 13,000 tons of obsolete pesticides are stored in 25 regions in Ukraine [1].

Storage facilities which were formerly used for storing pesticides are now old and weathered. Private vegetable gardens are often located on the territory of sanitary zones.

Thus the prohibited and toxic pesticides can easily reach the food supplies.

For example, the biosphere preserve *Ascania-Nova* is situated in the southern agroclimate region of the Khersonian district. It is a unique complex, which has virgin steppe, originating as a preserve in 1890. The steppe completely depicts the agricultural system which is typical for Ukraine. Dark-brown solonetzic soils, formed under fescue feather-grass are typical for the preserve.

In 1887 F. Falz-Fein created the irrigating botanical garden on the territory of the dry southern steppe in *Ascania-Nova*. The splendid Landscape Park was developed on a large area of 28 ha and preserved to the present time. Currently the Dendrological Park is the monument of the Garden and Park Art of the end of 19th century. The park is included in the Natural protective foundation of Ukraine as a component of the F. Falz-Fein Biosphere Reserve *Ascania-Nova* of the Ukrainian Academy of agrarian sciences. Its area is 170 ha. and it is the greatest irrigation park in Southern Ukraine and a concentration point for the wood vegetation and an introduction into the steppe zone. The Dendrological Park is also a scientific research institution. The development of ornamental plants is carried out at this institution. There are more than 600 exotic species of perspective woods which are recommended for planting of in the Southern steppe of Ukraine. The park is an object of ecological tourism. There are many exotic animals in the biosphere preserve.

To save the virgin steppe in its natural state, a buffer zone was created in 1978. The buffer zone is not solid. It is interrupted at a number of points, particularly in the location of the *Tishkove* sheep farm, the *Ascania-Nova* village, and at an agricultural airfield.

Inactive agrochemical storage and an agricultural airfield are located in the headstream of the hollow which flows into the Great *Chapelsky backstone*. For many years, reloading and repackaging of large amounts of pesticides were done there, which possibly caused the local soil pollution.

Currently, there are no pesticides in the storage; the warehouse itself is partially ruined. A wheat field and the runway are located at the distance of 10 meters from the warehouse. A monitoring study of the levels of HCH and DDT in the soil of storage's sanitary zone and airfield was carried out. The average concentration of DDT at a

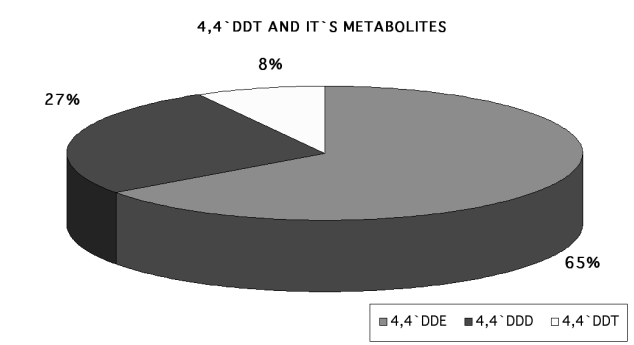


Figure 1: Correlation between concentration of DDT and its metabolites in the soils of arable lands

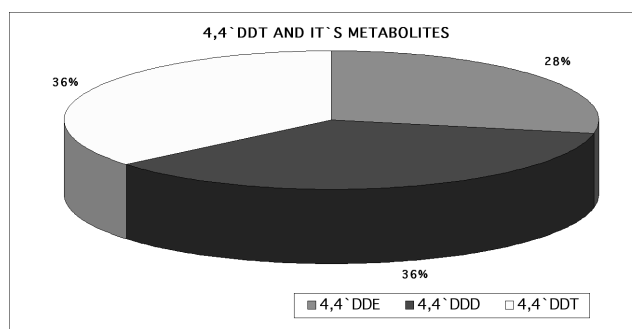


Figure 2: Correlation between concentration of DDT and its metabolites in the soils of the storehouse's sanitary zone

Location of the Storehouse	Concentration of the sum of isomers and metabolites of DDT (ug/kg)	Concentration of the sum of isomers of HCH (ug/kg)
Kyiv Region, Vasylkivskiy Area	16.0–647.0	7.0–826.0
Ivano-Frankivsk Region Sokyrnyanskiy Area	140.0–649.0	2.0–405.0
Territory of Biospherical Preserve Askaniya – Nova	52.8–1646.5	15.8–616.5
Hersonian Agricultural Institute of the South Region	24.3–234.7	12.4–89.1

Table 1: Levels of organochlorinated pesticides in the soil of sanitary zone of the pesticide storehouses

depth of the till recorded 1646.5 ug/kg while HCH averaged– 616.5 ug/kg. Thus, it is clear that the soil is highly polluted in such a way that it is dangerous for reserve territories and its protection being the task of all the human society.

The Institute of Agroecology and Biotechnology of the Ukrainian Academy of Agricultural Sciences, in the context of the program “Agroecological Monitoring and Sustainable Development of Agroecosystems”, conducted research on the levels of organochlorine pesticides during the period 2001 – 2002. During that project, arable soils and sites of former pesticide storehouses were investigated. Concentration of pesticides in the soils of arable lands of given regions did not exceed the acceptable values. The concentration of the remaining HCH ranged between 0 and 13 ug/kg while the total concentration of DDT and its metabolites was in the range of 0-35 ug/kg [2]. The percentage concentrations of HCH and isomers and metabolites of DDT are shown in Figure 1. Such correlation shows the absence of illegal usage of COP during the last years.

Also, monitoring of the prohibited pesticides of the soils in the sanitary zones of pesticide storehouses was carried out. Samples were collected by drilling holes at depth of 0-20 cm (plowing layer) around the four sides of the storehouse 5-10 meters apart. The samples were collected over the entire pollution zone.

The results of the investigation showed that the concentration of COP in the soil around the abandoned storehouses highly exceeds hygienic soil norms, adopted in Ukraine. (MPC of HCH – 100 ug/kg, MPC of DDT – 100 ug /kg). Therefore, the soil of sanitary zones of above-mentioned pesticide storehouses is the main source of pollution by persistent organochlorinated pesticides and requires immediate remediation.

Correlation between concentration of DDT and its metabolites differs from analogous correlation in the soils of active agriculture as shown in Figure 2.

In conclusion, the soil of the sanitary zones of the above-mentioned pesticides storehouses is the main source of environmental pollution of by persistent organochlorine pesticides and requires proper remediation.

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THE POTENTIAL OF APPLICATION OF NEW NANOSTRUCTURAL MATERIALS FOR DEGRADATION OF PESTICIDES IN WATER

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INTRODUCTION

It is known that majority of traditional methods of water treatment are little effective for purification of waters, especially drinking water, from hazardous impurities [1]. Recently some alternative methods of water purification from hazardous organic compounds have been studied.

New materials about the massifs of metal nanopoints, which are a united monolith consisting of the platform and nanosized cone elements rigidly fastened on it, have been recently developed [2]. Geometrical sizes of the cone elements can be varied approximately from 1 to 10 μm (height), from 0.4 to 3 μm (base radius) and from 20 to 2000 nm (radius of apex curvature). The surface concentration of the nanopoints constitutes from 10^3 to 10^8 cm^{-2} and can be varied directly as well.

The electron microphotographs of the massifs surface have shown that the massifs of nanopoints have the chemical activity without interference of an external field in reactions of degradation of organic solutes in water, and their activity essentially increases under the action of solar radiation and visible light [2,3].

Our work includes the first attempt to apply the new nano-materials for treatment of water polluted by pesticides (tachigaren and basagran), as well as by some other hazardous organic impurities (dyes and chlorocontaining compounds).

EXPERIMENTS

Two nitrogen-containing pesticides – tachigaren (3 – hydroxy – 5- methylisoxazole) and basagran (3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2 dioxide), as well as methylene blue (MB), thiazin red (TR), threechlorethylene and chloroform were used as models in this study. The experiments were carried out with 10^{-4} – 10^{-3} M in aqueous solutions of these compounds. All the reagents were chemically pure.

The nanostructured materials with the cone elements of aluminium, bismuth, nickel, gold, silver, palladium, vanadium, titanium, titanium dioxide and chromium were used for the study. The cone elements had the repeating geometrical sizes: 7 μm (height), 1.3 μm (base radius) and 50nm (radius of apex curvature), and the surface concentration of 107 cm^{-2} .

The devices with these materials were submerged in the solutions studied and irradiated by the solar light (Kiev region) in the first part of a day during summer months, and by the 100 W lamp at the distance of 25 cm during winter months. The ratio of the massif area to the volume of solution made up $1 \text{ cm}^2/\text{cm}^3$ in all the experiments. In order to exclude the action of outer fields, the solutions with the massifs of nanopoints were kept in darkness and in the shielding metal vessels.

Degradation of the organic compounds after some time was estimated by usage of absorption spectra, which were measured with spectrophotometer SF-26 in the UV – and visible fields.

RESULTS AND DISCUSSION

The analysis of the absorption spectra has shown that mainly oxidative degradation of organic molecules takes place. In case of chloro-containing compounds, the direct dechlorination of molecules occurs too as a result of slow electrons dissociative sticking.

The optical density of pesticides solutions at different wavelengths before and after the solar irradiation in the presence of massif with the copper nanopoints is shown in Fig.2. The molar extinction coefficients at the absorption maximum make up $3.0 \cdot 10^3$ and $2.45 \cdot 10^3 \text{ l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$ for basagran and tachigaren respectively.

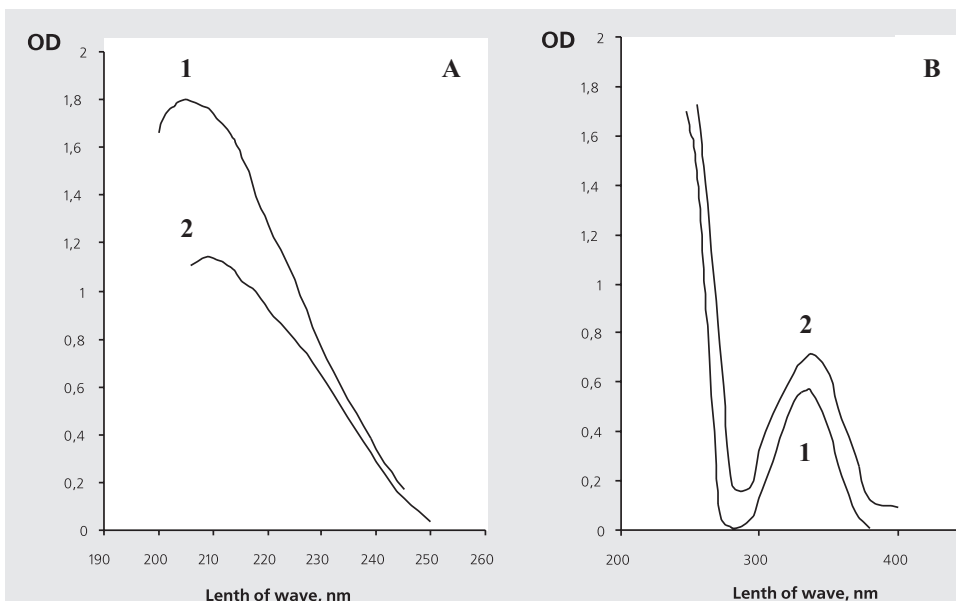


Figure 1. The optical density of $2 \cdot 10^{-4} \text{ M}$ pesticides solutions before (1) and after solar irradiation (2) in the presence of the massif with copper nanopoints: a) tachigaren, 5-hours irradiation; b) basagran, 10-hours irradiation.

Methylene blue								
Contact time, hours	0	2	4	6	10	16	18	25
OD at 650 nm	0.825	0.767	0.742	0.730	0.700	0.670	0.660	0.643
Thiazin red								
Contact time, hours	0			50			135	
OD at 505 nm	0.540			0.255			0.170	

Table 1. Change of optical density (OD) of dye solutions during the contact with the massif of copper nanoparticles in the dark.

Methylene blue							
Contact time, hours	0	1	2	5	10	20	30
OD at 650 nm	0.825	0.800	0.780	0.745	0.720	0.660	0.600
Thiazin red							
Contact time, hours	0	2	5	10	20	80	
OD at 505 nm	0.520	0.410	0.345	0.320	0.276	0.255	

Table 2. Change of optical density (OD) of dye solutions during the contact with the massif of copper nanoparticles under the action of solar radiation with the intensiveness of 0.078 W cm^{-2}

Material of nanoparticles	OD of dye solution	Material of nanoparticles	OD of dye solution
Gold	0.500	Titanium	0.660
Silver	0.540	Bismuth	0.680
Copper	0.550	Chromium	0.700
Nickel	0.575	Aluminium	0.740
Palladium	0.610	Titanium dioxide	0.730
Vanadium	0.625		

Table 3. Optical density of thiazin red solution after 30-min. contact with the massifs of nanoparticles made of different metals under irradiation by visible light (100W lamp). OD of feed TR solution was 0.745.

Contact time, hours	OD of CF solution at the wave length		OD of TCE solution at the wave length	
	200 nm	210 nm	200 nm	210 nm
0	0.280	0.115	0.690	0.465
1	0.260	0.105	0.625	0.423
2	0.240	0.100	0.570	0.380
3	0.225	0.098	0.525	0.350
8	0.150	0.083	0.260	0.172

Table 4. Change of optical density (OD) of TCE and CF solutions during the contact with the massifs of copper nanoparticles under the action of solar radiation.

It can be seen in the Fig.1 that feed pesticides solutions absorb the solar light mainly in the UV-range of spectrum. For tachigaren (Fig.1,a), the optical density decreases essentially after irradiation at the absorption maximum, when the wave length is of 205 nm. Besides, after irradiation the absorption maximum of the solutions moves to the long-wave range (210 nm). That confirms that the products of oxidative degradation of tachigaren are formed.

For basagran (Fig.1,b) the optical density of the solution increases at the absorption maximum after irradiation. That testifies to the destruction of basagran molecules to more simple ingredients and, as a result, the increase of solution molar concentration is observed.

The results of gradually optical density change of dye solutions with the lapse of time, which contacted with the massifs of copper nanoparticles in the darkness, are shown in

Table 1. One can see that degradation of the dyes, in the presence of massifs, takes place even in the dark, i.e. without interference of an external field. Methylene blue (MB) degrades more intensively than thiazin red (TR).

The chemical activity of the massif and, correspondingly, the rate of degradation of organic molecules essentially increase under the action of solar radiation and visible light. The data on the degradation kinetics of dye molecules in water under the action of solar radiation in the presence of massif of copper nanoparticles are given in Table 2.

Comparison of data of Table 1 and Table 2 shows that the optical density of MR solution decreases, for example, from initial 0.825 to 0,660 in 18 hours in the dark and only in 20 min under the action of solar radiation.

Comparative data of the effectiveness of the nanostructured materials made of different metals were obtained. Table 3 characterizes the relative effectiveness of massifs of nanoparticles made of different metals in reactions of thiazine red degradation. These results are confirmed in conditions of irradiation by the solar light, as well.

The line of chemical activity of the nanoparticles massifs of different metals in reactions of degradation of TR in water, as well as in content of other organic compounds studied is as follows: $\text{Au} > \text{Ag} > \text{Cu} > \text{Ni} > \text{Pd} > \text{V} > \text{Ti} > \text{Bi} > \text{Cr} > \text{TiO}_2 > \text{Al}$ (see Table 3). The massifs of nanoparticles of gold, silver, copper, and nickel have the highest chemical activity, i.e. they are the most effective for degradation of the organic impurities in water. The nanostructured materials of titanium, bismuth, chromium, titanium dioxide and aluminium make up a group of relatively low-active ones under such conditions.

The molecules of the chloro-containing compounds and pesticides, in contrast to the dyes, do not absorb the light in the visible field. However, these compounds degrade under irradiation by the solar light or visible light in the presence of massifs of nanoparticles. The data on optical density change of trichloroethylene (TCE) and chloroform (CF) solutions irradiated by the solar light in the presence of copper nanoparticles are given in Table 4.

The chemical activity of massifs of nanoparticles without interference of an external field, to our mind, is caused by existence of local heterogeneous fields at the apexes of nanocones in ordinary conditions. The regular shape of the nanocones, the excited electrons density at the nanoparticles with a small radius of apex curvature, and directed motion of electrons appearing in the volume of nanocones to promote this effect.

An essential increase of chemical activity of the massifs under the action of solar radiation or visible light is caused by intensification of the local heterogeneous fields as a result of incident radiation absorption. This fact was confirmed by measuring of optical properties of the metal nanoparticles massifs. As an example, the absorption spectra of silver nanoparticles and isolated silver nanoparticles on the transparent polymer support are given in Fig.2. The absorption spectrum of isolated silver nanoparticles coincides with the spectra, which are known from literature (for example [4]). However, the absorption spectrum of the silver nanoparticles is essentially different. In case of nanoparticles, an

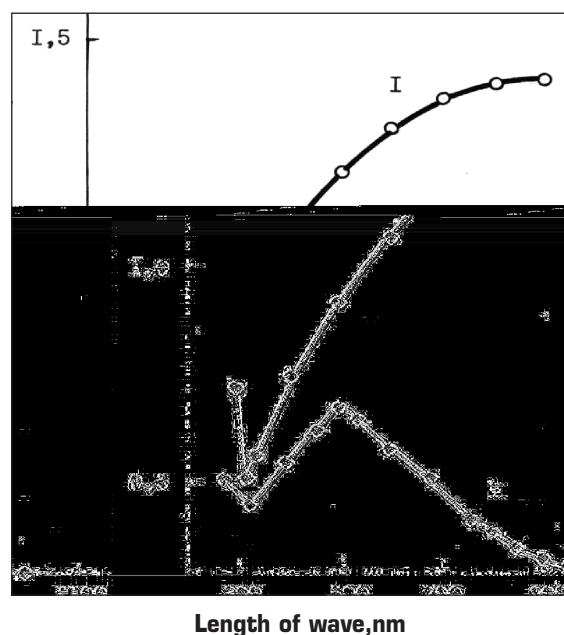


Fig.2 Absorption spectra of silver nanoparticles (curve I) and isolated silver nanoparticles (curve II)

increase of absorption while increasing the wavelength is observed.

As a result of intensification of local heterogeneous fields at the apexes of nanocones, generation of chemically active particles, namely, electrons, single oxygen, OH, HO₂, HO₃ radicals and others, takes place. The active particles interact with molecules of organic substances and oxidize them, in some cases, up to carbonic acid (gas) and water.

To render harmless hazardous chlororganic impurities in water, the low energy electrons play an important role. Owing to that the affinity of electron with the atom of chlorine (3.8 eV) exceeds the energy of dissociation of chlorine – carbon bond (3.5 eV), and effective dechlorination of chlororganic compounds and transformation of them to harmless products take place.

The observed effects and technological applicability of the method of hazardous wastes treatment and treatment of other waters containing organic impurities have to be studied in details. Simple devices including the nanostructured materials with the extended plane surfaces have been developed.

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SEARCH FOR NEW NON-HALOGEN CONTAINING CHIRAL PESTICIDES

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Agents of crop protection have a long-known history. In the beginning, they were generally inorganic compounds, often non-selective, active only at high application rates, and frequently toxic. For example, the legendary Bordeaux mixture presented the first modest weapons to be applied in the battle against diseases of potatoes and vines. Aiming of finding less toxic, selective organochemical active ingredients for crop protection applications, organized industrial research started during the 1930s, when DDT, 2,4-D, TMTD (Thiram) and Parathion (E 605) were discovered. During this period it has been established that chiral compounds are mostly active than non-chiral ones.

On the other hand, it has to be mentioned that in the last decade data about toxicity and persistence of halogenated pesticides were published.

Taking into account those observations, and based on our experience in chemistry of crop protection agents led to the synthesis of new non-halogenated chiral compounds. Synthesis of such compounds took place via combination of different types of fragments like cyclohexane, dimethylcyclopropane and triazole, imidazole or pirazole then bioactivity of such combinations were investigated.

Derivatives of azolymethyl cycloalkanol are of considerable interest among other fungicides that inhibit ergosterol biosynthesis. Most of these compounds are characterized by the presence of *para*-halogeno-benzylidene and alkyl groups at alpha, and alpha' positions respectively. A decision was made to synthesize such chiral compounds

containing analogous substituents in the molecule and replaces halogens with nitrones and *O*-methyloximes, then assays their antifungal activity [1-4]. The synthesis of the target compounds 4-9 is presented in Figure 1.

Several original procedures were developed for preparing compounds 2. Triazolymethylcyclohexanols 3 was obtained by opening the ring of the respective oxiranes 2 with sodium triazolidine.

At the final stage of this approach the condensation of aldehydes 3 with hydroxylamines went well and as a result, the target methyloximes and nitrones were prepared with mass production.

All of the prepared compounds showed low fungicidal activity in the *in vitro* assays with phytopathogen cultures and with infected tomato plants (phytophthora infection) and beans (gray mold). However, the compounds showed high efficiency against mildew on cucumber plants. In particular, 0.0025% of *O*-methyloximes 7, 8 or 9 suppressed disease evolution by 82%, 99.5% or 98% respectively, whereas the efficiencies of nitrones 4, 5 or 6 (at the same concentration) were 28%, 64% or 85%, respectively.

Synergism effect was seen in case of compounds 5 and 8. The diastereomers showed low antifungal activity than mixtures.

It is well known that enantiomerically pure compounds are usually more active than mixtures. Target enantioselective synthesis of different compounds based on chiral monoterpenoids is well known.

Then, another decision was made to synthesize heterocyclic analogues of widely used insecticides such as Permethrin and Decis, and to assay their insecticidal as well as fungicidal activity.

It could easily be observed that the available bicyclic monoterpene car-3-ene 10 consists of the same 2,2-dimethyl-1,3-disubstituted fragments and therefore it was selected for the aim of the present project.

The ester 11 was selected as the starting compounds for this approach and as a result the other types of chiral pyrazoles

Figure 1

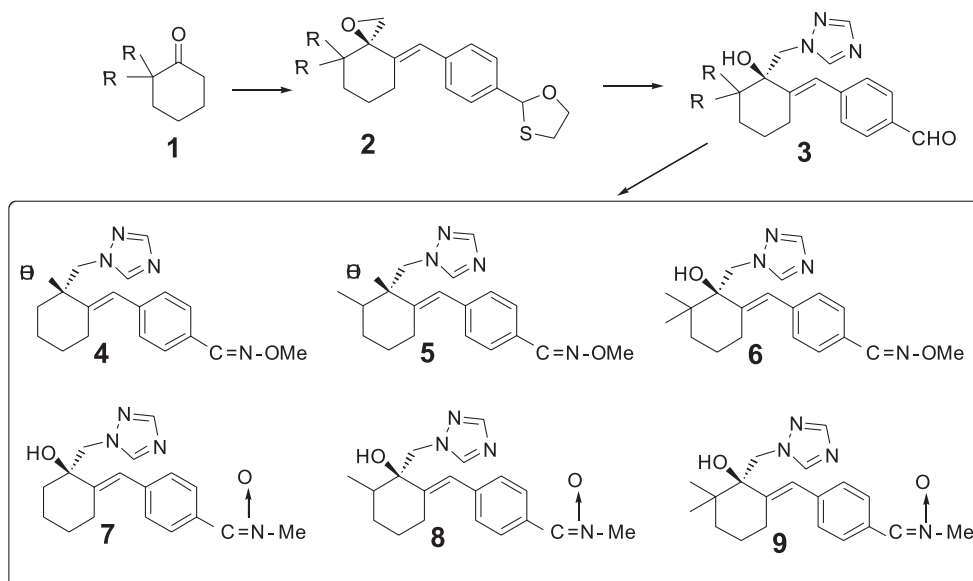


Figure 2

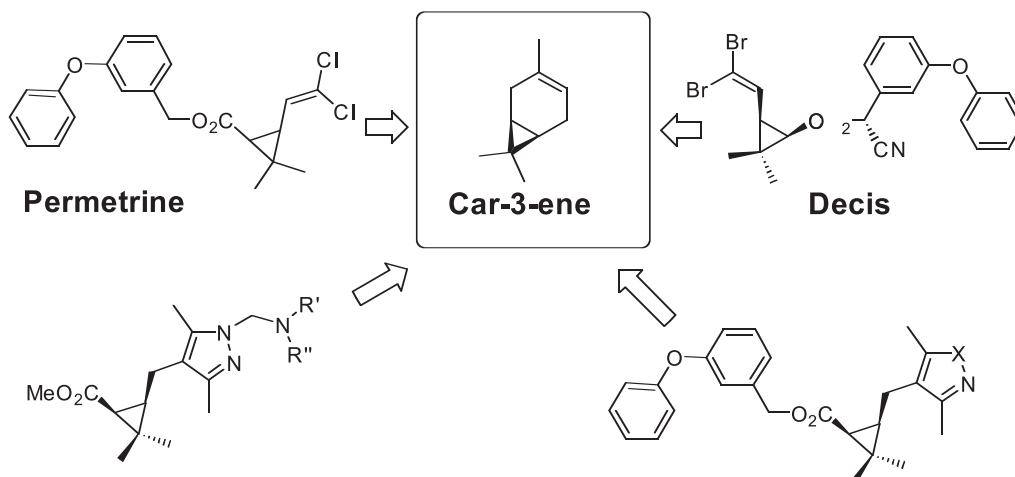
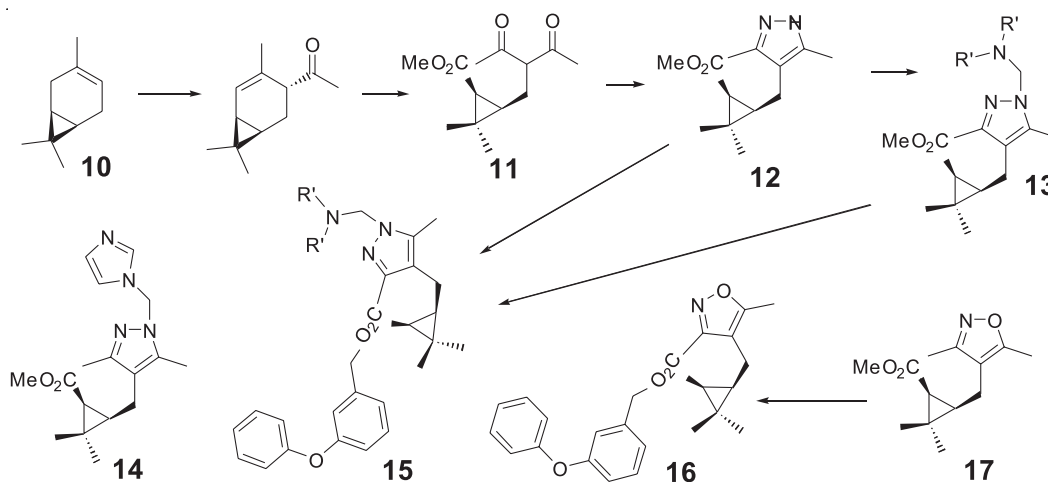


Figure 3



12-15 and izaxozole 16, 17 respectively were synthesized according to the schema in Figure 3.

All the compounds showed low insecticidal activity. The evaluation of the antifungal activity was performed on the pure phytopathogenic cultures *F.oxysporum*, *H.sativum* and *A.niger*. Those heterocycles that contained the pyrazole fragment were shown to be very potent fungicides in vitro.

SUMMARY

It was established that new non-halogen containing chiral compounds prepared from available sources could be used as pesticides.

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STATE OF PESTICIDES POLICY IN UKRAINE: CHALLENGES FOR EDUCATION AND GENDER APPROACH

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INTRODUCTION

Ukraine is one of the most ecologically adverse among European countries. Seventy percent of the Ukrainian population live on land deemed hazardous to human health for environmental reasons. Agriculture used to be one of the extremely polluted spheres of activities and its upon the environment has been devastating.

The key ecological problems in Ukraine, caused by agriculture, are: land degradation, soil and water contamination, and loss of biodiversity which all have seriously damaged not only the environment, but also the health of the population. The problems especially affect women and children, and have strongly contributed to the depopulation in rural areas that started in early 80th and continuous till today. The level of soil erosion, which is around 40% of total territory, could be considered as a national tragedy, and has lowered the contents of humus, nutrients and other essential components from the soil, including the humus-rich black chernozem; the annual loss of humus is 20 million tons, and the deficiency is 100 kg/ha. Soil is contaminated with chemical pesticides, heavy metals and acids, and radio nuclides. Pesticides residues pollute over 11% of cultivated land which primarily resulted from past practices [1]. Another strong environmental problem constantly observed in rural area caused by pesticides that could be divided into two main ones: problem with pesticide policy and using and problem with obsolete pesticides.

PESTICIDE USE IN UKRAINE – PAST AND CURRENT PRACTICES

Ukraine used to produce and consume high quantities of pesticides and chemical fertilizers. Their introduction began just before the Second World War and had expanded from the early seventies, continuing to increase to the early nineties. Ukraine, Moldova, Russia and Uzbekistan are accounted together for 72% of the use of pesticide products in the Commonwealth of former Soviet Union. The time of the most intensive application, specifically highly toxic and persistent organochlorines, were the years between 1986-1987, when the level of use reached 3-4 kg/ha of arable lands [1-2].

Many cases of pesticide poisoning happened during that period, but information was very restricted, and even now remains difficult to access. Recently information has come to light about massive levels of poisoning in the 1970s-1980s affecting women in five sugar beet farms in Cherkasska region, where polychlorcamphene was used to control Curculionidae and Chrisomelidae pests. The intensity of the treatment, the lack of protective clothing and

labels, and absence of safety information or training, were common conditions. Women were not warned that pesticides might affect them adversely.

Pesticide production and use have both dropped significantly during the last twenty years. In 1997, 24,000 tons of pesticides were applied, compared to 19,000 tons in 2001. The decrease results not from ecological concern but from economic realities because agricultural enterprises and farmers cannot afford to buy pesticides at previous levels and from the appearance of new pesticides on the market, that are active at considerably lower concentrations. The current application rate of pesticides is in the range of 0.7- 1 kg/ha of arable land. In 2001 Ukraine operates a pesticide registration system, which includes 378 pesticides. Organophosphates and synthetic pyrethroids are the most common groups used for insect pests: by weight diazinon is the most applied, followed alpha cypermethrin and deltamethrin. Among herbicides 2,4 D is the most common [2].

There has been a general decrease in the toxic residues found in soil and food, with a reduction in the frequency of detection organochlorines in soil of 71% and in crops of 83% since the peak period of chemical application.

Registration of pesticides and fertilizers, whether local or imported, is compulsory and is the responsibility of the Commission of Chemical Security at the Ministry of Ecology. Two main laws regulate pesticide policy and consumption: the Pesticide and Agricultural Chemicals Law, adopted in 1996, and the Crop Protection Law, adopted in 1998.

The past twelve years has seen some changes in the monitoring of pesticide consumption. In the past this was under the remit of the Ministry of Agriculture, which has subdivisions in all regions in Ukraine. The regional subdivisions kept records of use which the Ministry of Agriculture estimated pesticide requirements. The Ministry lost this responsibility in the mid-1990s and since then consumption requirements have been left to the market. The Protection Association now partly take on the function of estimating requirements which has 49 members from foreign companies, local producers, and pesticides dealers and distributors in Ukraine and thereby sometimes promotes the interests of foreign companies. The Ministry of Ecology and its local branches are responsible for the control of contamination of the environment by pesticides and product of their decomposition.

OBsolete Pesticide Problem in Ukraine

This problem is continuing to be among the most serious one in the country. Pesticides residues, including highly toxic and persistent DDT and HCH can be found in the soil, water and crops in all regions of Ukraine. The principle source of soil pollution is misuse of pesticides and mineral fertilizers and improper storage of pesticides.

A significant contributive factor to contamination is the existence of obsolete pesticide stocks, which are leaking leak through the soil into ground water. Total stocks exceed 13,520 tons in 1998 (see Table 1) and are found in 25 regions, although the amounts vary considerably from region to region. The largest, 1,820 tons, are in the Kiev

indices	Group of pesticides in storages		
	Prohibited pesticides	Deteriorated pesticides	Unknown pesticides
Number of chemical products	58	165	–
Weigh in tons	3,428	1,509	8,582
Total weight in tons		13,5704	

Table 1. Obsolete pesticide stockpiles in Ukraine (data of the Ministry of Ecology and Natural resources , 1998)

region, posing extreme dangers for the three million residents of the capital city. Most of these stockpiles accumulated in the 1970s from temporary storage, and the conditions have deteriorated dramatically. Many are stored outdoors, and their containers are broken and leaking.

According to the latest data of the Ministry of Ecology, in year 2003 the total amount of Obsolete Pesticides in Ukraine is over 20,000 ton and around half of those is mixture of pesticides or substances with unknown chemical formulas.

In spite the fact that the majority of highly persistent and toxic pesticides were banned in Ukraine in the 1980s, some remain in use. Outbreaks of pests like locust (*Locusta migratoria*), cutworms (*Agrotis segetum*), stem and seed weevils (*Curculionidae*), wireworms (*Elateridae*) and grubs (*Melolonthidae*) have occurred in the last six years. To suppress deal with these, 1,000 tons of obsolete pesticides have been used, including methafose 40% , BCH 25%, Dursban 40,85 c.e. (chlorpyrifos) .

PLACE OF EDUCATION TOWARD THE SUSTAINABLE AGRICULTURE

Ukraine is taking its first steps towards the implementation of sustainable agriculture strategy and faces a lot of challenges. It is important to make the educational and institutional changes necessary to meet challenges. University teachers should not be satisfied with just traditional format of teaching and remember they train professionals to work in rural community. Ecological awareness raising and education regarding to the promotion of good agricultural practices among different stakeholders group should be enforced as well as unformal education should become the equitable part of the continuing educational process. Non-governmental organizations' participation is an important component of informal continuing agricultural education [3-4]. However public support for agricultural higher education in Ukraine is still weak.

Traditional agricultural university education cannot meet future rural challenges on management, conservation and agribusiness alone. Agricultural educational system should make leap from simple universities education to a greater emphasize on non-formal adult education in order to influ-

ence a wide range of stakeholders including those in academia, in farming and non-farming rural areas, policy makers and the private sector.

Public organization "Center of Sustainable Development and Ecological Education " was created in 1999 in order to disseminate principles of sustainable development in Ukrainian in general and in agriculture in particularly and has joined researchers, students, farmers and professors.

The numbers of research activities regarding an obsolete pesticide awareness raising taking in consideration gender issue have been accomplished recently and have a several objectives:

- Describe status and trends in obsolete pesticide use in Ukraine;
- Identify sectors involved, those that should be involved, and changes required to provide enabling pesticide policy;
- Identify if there is gender equality in the rural areas and are the health risks from intensive agricultural practices greater for women than for men;
- Relevant what role women play in implementing of sustainable agricultural principles;
- Strengthening of the capacities of farmers, their communities and organizations, enchasing active participation of women as partners, decision makers and beneficiaries

A GENDER VIEW ON THE USE OF PESTICIDES

Women constitute the majority (54%) of the rural population in Ukraine, and play an important role in agricultural labor force, as well as in production and preparation the food for their families. Yet their position is grossly unequal within society which could be illustrated by such data [5] :

- Women's wages are only 70% of that of men;
- More poor households are headed by women;
- More than 43% of rural unemployed are women;
- Of the women relevant education, only 5% are directors of the agricultural state farms, while of men with similar education, 50% hold a supervisory post;
- On private farms, only 173 women are in managerial positions;
- Employment conditions are worse for women, who undertake 65% of agricultural labor;

The question	Yes (%)	No (%)	Not sure (%)
Do you think pesticides are seriously injuring your health?	13 (26)	27 (54)	10 (20)
Have you observed any illness due to pesticide exposure?	5 (10)	41 (82)	4 (8)
Do you know the health effects caused by pesticide exposure?	15 (30)	25 (50)	10 (20)
Do you think there could be a relationship between breast cancer and pesticide exposure?	6 (12)	42 (84)	2 (4)
Is it important to wear protective clothing?	23 (46)	16 (32)	11 (22)
If faced with an a serious pest threat to harvest, is it justifiable to use an obsolete pesticide:			
(a) on a large agricultural enterprises	42 (84)	13 (26)	6 (12)
(b) on a small farm	17 (34)	2 (4)	20 (40)

Table 2. Results of survey of 50 women about risks that pesticides pose for their health, Borodianka, Kievsk region, 2001 (Women interviewed = 50)

- With domestic responsibilities, women in rural area work approximately 16 hours per day;
- Women in rural community are widely involved in pesticide application.

A survey of 50 women in childbearing age was done by Center's member to investigate the extent to which women understand the routes of exposure and the unique potential impacts their health. All those interviewed apply pesticide application on the family farm (table 2). Table 2. Results of survey of 50 women on risks that pesticides pose for their health, Borodianka, Kievsk region, 2001

The questionnaire indicates that Ukrainian women are not strongly concerned with pesticide exposure, which is routine, and little attention is paid to occupational risk factors. Information on pesticide poisoning is notoriously under-estimated, however studies indicate that pesticides exposure has been associated with cancer of breast, testes and ovaries

CONCLUSION

The important role of public participation, NGOs involvement and strengthening the women's role in promoting environmental awareness and stimulating the legal and institutional frameworks need to present and promote principles of sustainable agriculture for rural communities [5]. There is a great need for public awareness and information dissemination regarding the risk to health from environmental contamination with pesticides using and obsolete pesticides impact. It is important to make the educational and institutional changes necessary to meet challenges. Ecological awareness raising and education regarding to promotion of good agricultural practices among different stakeholders group should be enforced. In agricultural universities new courses balanced scientific approach and impute from humanities including environmental ethics and socioecology should be introduced to the curriculum.

Understanding of the importance of gender issues in promotion of ecological agriculture should be emphasized in professionals training [6]. Agricultural professionals for XXI century should combine strong scientific background with humanism and abilities to work in the social environment. To achieve this goal the partnership and collaboration are needed between different agricultural education systems and private sector as well as with a range of other stakeholders including NGO, farmers' organizations, and consumers.

Women's role in the promotion of sustainable ecological agriculture should be always taken in consideration. It should provide the more active participation of women, as partners, decision makers, educators and beneficiaries [7].

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ECOLOGICAL ASPECT OF POLLUTION OF ENVIRONMENTAL OBJECTS BY PESTICIDES IN THE CRIMEA

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The Crimea by its nature is unique resort territory of the World. The unity is presented by its picturesque mountain landscapes covered by thick forests full of various flora and fauna. The forests are situated on the Black Sea Coast in soft temperate climate; lakes are rich with salt water and dirt that is why the Crimea may be called the resort. The Crimean wealth is also in its soils in which it is possible to yield great crops of fruit, vegetables and special sorts of wheat. There are also many rivers, which flow along fertile valleys to the sea. However the solid and liquid wastes of industrial enterprises, dumps, intensive agricultural activities of fertilization and protection of plants and also household waste produce the great anthropogenic effect on the natural resources of the Crimea.

The Crimean land fund is of 2608.1 thousand hectares, 1857.7 thousand hectares of which are agricultural fields (that is 71.2% of all the area), 359.1 thousand hectares are subjected to chemical treatment.

One of the acute problems of the Crimean agriculture is the usage of pesticides. The most widely used among them are HCH Reglon, Bazagrane, Fundasol, Karate, BI-58, Aldrin, Heptachlor, 2,4-D, Atrazin and others.

The intensive usage of pesticides created the preconditions for their accumulation in soils and also in other objects of environment (in freshwater (reservoirs) lakes, vegetable top-soil, sea water, water inhabitants etc). The ability of accumulation in living organisms is directly dangerous for human health.

The analysis of pollution distribution in natural surroundings, its migration cycles and transformation in biosphere is of great importance for estimation and forecasting of ecological after-effects of the anthropogenic factors influence. General pesticide pollution of atmosphere, hydrosphere and bioorganisms shows that this substance is in permanent movement from one natural sphere to the other.

At present there is the danger of level increase of food pollution by pesticides, which is connected with violation of order and dose of their application. The threat of environmental pollution is connected with irregular keeping, pesticides accumulation and the absence of their harmless rendering technology.

According to [1] in 1998 there were 684.8 tons of toxic substances at chemical stocks, 337.3 ton of which were prohibited. At present these chemicals are not annihilated because of the technology absence.

The storage of pesticides is carried out in 300 stocks situated in different farms. But the conditions of keeping frequently do not correspond to the requirements of the

Ukraine law "About the pesticides and agrochemicals application, their transportation and storage".

Many years of observation in the region indicate the influence of pesticides on the whole ecological system.

The purpose of our research is to study the dynamics of pesticide accumulation in the soil (using the data of agrochemical monitoring), to define their effect on the quantity of agricultural products, the influence of the most badly decomposed pesticides on the environment in the Crimean regions, which have the special importance as a resort (especially Saki region).

The behavior of pesticides in soils depends on many climatic factors. As there is practically no soil self-purification, the toxic substances have such a tendency to accumulate. This process leads to the constant change of chemical composition of the soil, violation of the agrochemical environment and organisms' unity and also pollutes the foodstuff. According to [1] 2295.4 tons of pesticides (2.1 kg per hectare) were used in 1998 in the Crimea.

According to data of the center "Krymgosplodorodie" there was the best situation when they used the groups of 2,4-D and triazines (2,4-D, Atrazin), which were kept in soil for 7-24 months after the cultivation. When 2,4-D was used over 2730 hectares and Atrazin - over 145 hectares the residual quantities were not seen in fruit and vegetables in 2002. According to soil-agrochemical monitoring the results of the determination of pesticide residual quantity in wheat of soft sorts showed that in 2000-2001 there were found the residual quantities of HCH and DDT in maximum concentration limits, which equal 0,5 mg/kg and 0,02 mg/kg correspondingly, especially in Simferopol and Saki regions.

The results of residual quantity definition of the most dangerous pesticides in food wheat of soft sorts growing in the Crimea are given in Table 1.

However, if the problem of the most dangerous pesticides accumulation at agricultural plants can solve the problem of pesticides pollution of lakes and soils, it is very acute for the development of resorts, as well as small quantity of resorts, as even small quantity of chemical substances annuls the use of salt-water and dirt for cure. In particular, we investigated the accumulation dynamics of HCH, DDT, DDD and DDE in waters of Saki salt lake, which is unique in its chemical composition for the cure of many diseases.

The Saki dirt cures:

- 10 disease of osseous-muscular system and conjunctive tissue, rheumatic arthritis, osteoarthritis;
- 11 residual traumatic phenomena and intoxication of the central nervous system;
- 12 disease of the peripheral nervous system, jugular shoulder-blade inflammation, neuralgia of intercostal nerves;
- 13 gynecological diseases (women's diseases), infertility;
- 14 diseases of genitals; prostate gland;
- 15 diseases of the throat;
- 16 skin diseases;
- 17 disease of the dental-maxillary system.

Chemical Composition of the Saki Dirt.

- 10 water – 43.05%
- 11 dissolved salt – 5.89%

№		resQuantity mg/kg (not more)					
		Aldrin	Heptachlor	HCH	DDT	Hexohloran	
		MCL	Not allowed	Not allowed	0.5	0.02	0.2
Crop 2001y.							
1	Sakisky		Not discovered (n.d.)	n.d.	Less than 0,00001	Less than 0,006	---
2	Pervomaycky		n.d.	n.d.	Less than 0,00001	Less than 0,006	---
3	Chernomorsky		n.d.	n.d.	Less than 0,05	---	---
4	Simferopolsky		n.d.	n.d.	Less than 0,05	---	---
Crop 2002 y.							
5	Kirovsky v. Partisani		n.d.	n.d.	Less than 0,05	---	---
6	Belogorsky		n.d.	n.d.	Less than 0,05	Less than 0,05	Less than 0,007
7	Simferopolsky		n.d.	n.d.	Less than 0,05	Less than 0,05	Less than 0,007
8	Balaclava		n.d.	n.d.	Less than 0,05	Less than 0,007	Less than 0,001
9	Pervomaysky v. Gvardeyskoe		n.d.	n.d.	Less than 0,05	---	---
10	Chermorsky		---	n.d.	Less than 0,01	Less than 0,01	---

Table 1. The Residual Quantity of Pesticides in Food Wheat of Soft Sorts ($n=3$, $P=0,95$)

- 12 colloidal complex – 10.96%
 13 crystal part – 40.10%
 14 General Properties.
 15 specific weight – 1.6 g/sm³
 16 mineralization of pores solution – up o 200 g/l
 17 humidity – 34-42%
 18 resistance to shift – 200-400 din/sm²
 19 thermal heat capacity – 0.5 cal g/grad
 20 Ox/Red potential – minus 250
 21 pH – 7-7.5
 22 the general quantity of microorganisms – up to 500000 in gram
 23 pathogenic macroflora is not egested
 24 the radio-active pollution is absent
 25 the sanitary state is in norm limits by estimation criteria
 26 radius of growth delay zones in relation to staphylococcus culture – up to 20 mm.

Chemical Composition of Dirt Solution.

Cations g/l	Anions g/l
Potassium – 1.82	Chlorine – 73.78
Sodium – 37.23	Sulphate – 14.05
Magnesium – 8.342	Hydrocarbonate – 0.488
Calcium – 1.08	

Saki salt lake is on the western coast of the Crimean peninsula and belongs to lakes of estuary. At present Saki medical dirt deposit is surrounded by dangerous for environmental protection infrastructure.

According to “Regulation on protection sanitary areas of water objects”, it is necessary to reveal all the pollution sources in sanitary protection zones. [2]

It's common knowledge that pesticides pollution of the surface lakes waters is mainly the result of flowing out from agricultural fields.

There are many village fields of Mikhailovka, Orehovo and cottage places near Saki lake, which provoke organic chemical pollution of surface and underground waters.

As the result of investigation the pesticides were discovered in soil samples (table 2).

HCH was not revealed either in the Northern or Southern banks of the lake, but DDT and its derivatives, were in all samples of the soil. However there is no excess of pesticide maximum concentration limit in all samples of the soil.

While investigating the pesticide concentration in salt-water and silt they were found in all five samples of salt-water (by perimeter of the lake). HCH, DDT, DDD, DDE concentration of about 10-5-10-6 mg/l was marked. This is less than maximum concentration limit, but in spite of this

The place of selection	γ HCH, mg/kg	DDE, mg/kg	DDD, mg/kg	DDT, mg/kg	Sum DDE DDD DDT, mg/kg
Northern bank	0.0013	0.0053	0.0011	n.d.	0.0077
Southern bank	n.d.	0.0005	n.d.	0.0006	0.0011

Table 2. Pesticide Concentration in the Soil of Saki Lake Territory

the salt-water quality has deteriorated and became dangerous for health as pesticides can penetrate through the skin and concentrate in fat tissue [3,4].

The organochlorin pesticides concentration of 10-3-10-4 mg/kg was revealed in many silt samples, which testifies to their concentration in silt. There was no concentration of DDT in some samples as this substance has not been used for more than 10 years, but there was concentration of 10-3-10-4 mg/kg of its derivatives DDE, DDD.

Saki Hydrological station researches showed the vertical and horizontal migration of pesticides in all surrounding objects (in surface flowing, silt, channel, air and soil).

The analysis of investigation done confirms the danger of concentration of often used pesticides in Crimean lakes that makes the medical quality of unique dirt worse and creates the threat to health as pesticides are too dangerous for people.

PILOT SURVEYS OF OBSOLETE PESTICIDE STOCKS IN SLOVAKIA AND HUNGARY

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ABSTRACT

As a result of the economic transition in the Slovak Republic, many former collective farms have been privatised or ceased to exist. The consequence of this is that stocks of obsolete pesticides are often left under poor control and management, and therefore pose a severe and direct threat to human health and the environment. A pilot project conducted in 2002 by the Environmental and Cultural Association of the Ipel' River Watershed – Ipel' Union NGO in cooperation with the Reflex Association in Hungary and with the assistance of the Dutch Ministry of the Environment, has shown that the responsible authorities have no comprehensive list of the locations of these stocks.

The strategy used in the pilot project is characterised by the cooperation of national and local authorities, agricultural organisations and NGOs. For efficiency and safety reasons, the survey phase was separated from the expert inventory phase. The pilot project resulted in a list of 63 storages in the pilot region in Slovakia (229 municipalities out of the total 2883).

Furthermore, a protected web-based database for documenting data about the locations and storage conditions of the found stocks was produced, with a view to the prioritisation of treatment activities. Also a manual has been prepared for the implementation of surveys in other regions and countries in Central and Eastern Europe.

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The survey method in Hungary was a different one. While in Slovakia a "quick-sweep" was done by 20 field-workers, in a period of 2 months, in Hungary five NGO field workers conducted the survey on a part-time basis, and the project period was 9 months. The survey in Hungary started with the training of fieldworkers in September 2002, after which the actual field research began in December in 410 municipalities, and was completed at the end of May 2003. The results of the pilot survey have not been completely analysed yet. Up to the 15th May 2002 there were 46 stocks of obsolete pesticides localised in 158 municipalities of Hungary.

As part of the project a small number of demonstration clean-ups were organised as well. In Hungary five demonstration clean-ups were conducted between November 2002 and March 2003, in five municipalities of the survey region. By this activity more than 7000 kg of obsolete chemicals were incinerated in the incinerator of Győr (HU).

In Slovakia the situation is more difficult. Several disposal companies and incinerators were addressed by the Ipel' Union, but according to the data of the Guidance Committee of the Dutch Ministry of the Environment none of them is up to European standards, thus no appropriate techniques for the disposal of obsolete pesticides have been found so far. According to the recommendations of the Dutch Guidance Committee the problem of treatment of obsolete pesticides should be handled on a regional scale, which means that the chemicals identified in Slovakia should be incinerated in Hungary, in Győr or Dorog. For this regulations of the Basel Convention should be followed, according to which the agreement of the authorities of the recipient country is necessary. The discussions with the competent Hungarian authorities are in process, and the demonstration clean-ups are planned to be completed in the first half of the year 2003.

The results of the pilot inventory provide a strong basis for the preparation of a proposal for nation-wide inventories and expert inventories of the localised stocks as well as of proposals for disposal.



Stock of obsolete pesticides in Bielovce, Slovakia



Stock of obsolete pesticides in Bielovce, Slovakia

ORGANISATION OF THE PROJECT

Identify and request funds

SK: Partnership NL - SK, 30.000 EUR, survey in 1 province

HU: NL – HU Partnership for Accession, 50.000 EUR, survey in three provinces + design and management of a web-based, password protected database

Set-up of organisational structure

SK: Coordination: Ipel' Union Field work done by 20 student fieldworkers
Supervisory Board: Ministry of the Environment, Ministry of Agriculture

HU: coordination: Ipel' Union + Reflex Association
Field work done by 5 NGO field workers
Supervisory Board: Ministry of the Environment, Ministry of Agriculture

Development of materials

- Inventory protocol
- Training manual
- Storage form – conform FAO
- Information letters for target groups
- Database analog to storage form (www.obsolete_chemicals-cee.org/chembase)

Training of field workers

SK: Date: July 2002

Participants: 20 students

Topic: background of obsolete pesticides

After theoretical part field trip to practice learnt skills

HU: Date: September 2002

Participants: 5 NGO members

Topic: background of obsolete pesticides + results of Slovakian pilot

Information campaign

- Information letters + self reporting forms to municipalities, NGOs, agricultural farms
- Information about the project in local and national media

Conducting pilot inventories

- Combined approach – “top-down” and “bottom-up”

SK: 229 municipalities

Focus: only locations and storage conditions

Time of survey: July – August 2002

HU: 410 municipalities

Focus: only locations and storage conditions

Time of survey: September 2002 – June 2003

Demonstration clean-ups

- Goal: to facilitate ongoing pilot surveys

SK: Funding by UK DEFRA

1-3 planned locations

Coordination by Ipel' Union

HU: funding by UK DEFRA

5 locations coordination by Ipel' Union + Reflex Association

SURVEY RESULTS

Slovakia

- 63 stocks localized as opposed to nine on Government list
- Quantity over 50 tons
- Conditions of storage: in most cases not sufficient

Hungary

- Data analyses not completed yet – up to 15th May 2003: 46 stocks
- Governmental information inaccurate
- Quantity: 46 tons of OP + 330 m³ packaging material
- Conditions of storage: 14 not sufficient



Demonstration clean-up in Naszály, Hungary



Stock of obsolete pesticides in Vel'ka Calomija, Slovakia

OBSOLETE PESTICIDES AS PERSISTENT ORGANIC POLLUTANTS: DISPOSAL TECHNIQUES

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The huge amounts of obsolete pesticides (OP), most of them persistent organic pollutants (POPs), stockpiled in Ukraine, call for proper disposal and destruction techniques. However, most of the methods developed are not versatile, require complex and expensive equipment, and do not solve the problem of empty containers and packaging materials.

As a result only one technique for hazardous waste destruction is used worldwide: high-temperature incineration. Its advantage is the possibility to destroy practically all kinds of organic waste. Its disadvantage is almost inexorable dioxin formation and necessity of transporting large amounts of hazardous waste to the location site, *something* which leads to protests from the local population and NGOs.

There are no such facilities in Ukraine and their construction is not planned for economical and social reasons.

Eco Logic Inc. Canada developed a new method for safe destruction of POPs, the so-called gas-phase chemical reduction. In this high-temperature process, hydrogen reacts with POPs forming mostly methane and hydrogen chloride with small amounts of light hydrocarbons. Contrary to incineration processes there is no oxygen atmosphere and therefore dioxin formation is effectively prevented. Currently there are two demonstration plants in operation in Japan and Canada and two semi-mobile plants should be operational in Japan and Slovakia by the end of this year. At present detailed data are unavailable although we can guess that the cost of such a plant may be comparable to the usual cost of a modern semi-mobile incinerator facility, i.e. a few million US dollars.

Taking into account *also the* current economic and social situation in Ukraine, we propose some short-term solutions to the obsolete stockpiled pesticides *problem*.

A good way of temporarily solving the problem is generation of interim storage sites where OP can be stored under controlled conditions. In this case, though, it is necessary to develop techniques and equipment for safe repackaging and further storage of OP. Also, the opportunity of easy handling and unpacking in case of final disposal must be considered. The problem of used containers must be addressed as well.

Analysis shows that presently no versatile packing material for OP repackaging and interim storing exists. In Ukraine polymer, metal, and reinforced/polymer-impregnated concrete containers are presently in use.

Advantages of plastic and metal containers are the following:

- low costs;
- mobility;
- no further OP mixing when repacking;
- easy cleanup or destruction if necessary;
- *possibility* of repeated use.

The main disadvantages are:

- easy illegal access;
- high risk of improper use.

This requires stringent security measures at storage sites. It should be noted that such repacking is only justified given the availability of proper stores that comply with all safety requirements. The storage site must be secured and guarded as well as equipped with a monitoring system.

Concrete containers for interim storage have one advantage: their design prevents illegal access. Nevertheless, they too require establishment of a proper storage facility with safety measures.

Their disadvantages are:

- high costs;
- great capacity and weight (when working with small amounts of OP, mixing becomes inevitable);
- no quality guarantee;
- unsuitable for liquid formations of OP;
- can hardly be used repeatedly or destroyed.

Some work on OP repackaging into containers of various kinds has been done in Ukraine. In Donetsk, Kherson, Lviv, Odessa, Kyev and other regions, container storage sites have been built. The overall bulk of OP repackaged is about 2000 tons.

A storage site in Lozovaya, Kharkov region, was restored, and about 150 tons of OP were repackaged into polymer and metal containers under a joint Danish-Ukrainian project "Elimination of risks related to stockpiled obsolete pesticides in Ukraine".

The above-mentioned methods, however, must be considered only as temporary measures. Presently, no OP utilization techniques are available, which is why the only solution to this problem is their complete destruction.

One suitable method for OP destruction is biological conversion under anaerobic conditions, the so-called composting. Since Soviet times, composting has been recommended for rendering organo-phosphorus pesticides, as well as phenoxyacetic acid derivatives, harmless. Our research has shown that under certain conditions all OP can be composted.

The most common method for OP destruction implemented worldwide is cement rotary kiln incineration. Its advantages are:

- very high operating temperatures (1,300-1,400 °C);
- sufficient (gas) residence time in the incineration zone (over 7 sec);
- acidic gases from pesticide destruction are absorbed in the clinker;
- affinity between clinker constituents and inert constituents of pesticide formulations;
- pesticide destruction occurs in liquid oxygen deficient

phase, whereby the possibility of dioxin formation is greatly reduced;

- empty pesticide containers can be destroyed in the kiln (with the possible exception of concrete containers).

Implementation of this method in Ukraine is impeded not by technical or economic problems, but rather by the difficulties associated with long-distance OP transportation from storage sites to cement plants. Human issues are also significant, since most of the personnel are unwilling to deal with hazardous chemicals. These can be solved by first coating pesticides and producing granules. The granules can be easily fed into the cement kiln. Destruction takes place inside granules under anaerobic conditions, thus preventing dioxin formation.

Given that large amounts of OP are stored at small sites, it seems reasonable to use mobile pyrolysis facilities for OP destruction immediately at storage sites. The pyrolysis method for OP and PCB destruction was developed and implemented by Elga Ltd., Shostka.

The Elga process consists of two phases: alkaline hydrolysis and low-temperature pyrolysis. In the first phase the waste being destroyed is mixed with solid lime and caustic

soda solution and heated at 200-250 °C in a hermetically sealed stainless steel reactor. In the second phase the temperature is raised to 500 °C and the pyrolysis is continued as long as gasses are emitted. Then the gases are cleaned from contaminating substances and released into the atmosphere. Solid residues do not contain organic substances and can be safely landfilled.

The advantages are:

- POPs destruction occurs under anaerobic conditions, thus preventing dioxin formation;
- low energy consumption;
- POPs can be destroyed immediately at the site, avoiding risks associated with any kind of transportation and interim storage;
- low capital and operating costs that can be afforded by local authorities;
- these mobile facilities can later be used for destruction of other hazardous wastes, including PCBs.

Using this method more than 100 tons of OP has been destroyed.

ECOLOGICAL ASPECTS OF APPLICATION OF BIOLOGICAL PLANT PROTECTION AGENTS AS ALTERNATIVE OF CHEMICAL PESTICIDES

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The global contamination of biosphere causes reasoned anxiety about possible break in ecological processes and ecological balance in separate areas of biosphere. The potential danger is connected with synthetic artificial substances, which were released in the environment as a result of human economic activity. It is the main reason why protection of environment is one of the most important and acute problem. The goal to work out and to use an effective and safe method for plant's protection against harmful organisms is one of the key chain within this global problem.

Protection of plants from pests and illnesses is not only one of the most important links, but one of inevitable links in complex of measures for agricultural production augmentation. Today a chemical method still occupies the leading place in plants protection. In many cases it permits to repress comparatively rapidly and effectively the development of harmful organisms, preventing the harvest losses.

Pesticide's using gives a high economic effect, but also it has caused serious negative phenomena. The practice of chemical pesticides application along many years has

showed that many of them are poisons with broad action spectrum. Pesticides can be accumulated and circulate in the environment, they can destroy natural biocenosis, be dangerous to animals, be injurious to human health.

The strategy of plants protection has changed under the influence of negative impact of pesticides. It leads to limitation of chemical preparations application and usage of integrated plant management based on high agrotechniques and application of biological and selection methods.

The application of biological preparation is based on using microorganisms, created in the natural way, in integrated pest management is one of way to decrease pesticides usage same time increasing a ecological safety of plant protection against pests and illnesses. There are microorganisms – antagonists of plants illnesses or pathogens of pests.

The microbiological method of agricultural pest control is based on using relations existed in nature between pathogenic microorganisms and receptive to them macroorganisms. It provides a specific action of method. The different microorganisms are used. First of all the natural enthomopathogenes are used in this method. They are such infectious agents, which can cause an epizootic in population of pests, repressing their quantity to economic undangerous level. And it is not dangerous to other species of animals and plants. The specific pathogens of the mouse-like rodents, causing epizootic among them, are also widely used.

The number of microbial preparations – insecticides, rodenticides and fungicides (bitoxibacilline, bactorodencide, phitoverm, trichodermin, kleps and oth.) are worked out and used in Ukraine on the base of microorganisms. Except of

Num-ber	CHEMICAL PESTICIDES	BIOPREPARATIONS
11	High biological effect (swarms of harmful organisms)	Lowering of the number of harmful organisms to economically undangerous level, which is ecologically important in particular
22	Relative simplicity of use	High electivity of action
33	Long expiration date of preparation	Do not disturb natural biocenoses
44		Non toxicity for warm-blooded organisms
55		Possibility of reproduction and dissemination of infectious preparation agent in nature
66		Non toxicity for unpurposed organisms
		Lack of accumulative action
88		Application of biopreparation lowers the chemical loading of the environment
99		Does not worsen the soil fertility
110		Natural ways of decomposition in nature
III		Cost of production of biopreparation
		is cheaper, than pesticide one

Table 1. Comparative list of advantages of biopreparations and chemical pesticides

microorganisms (the main working ingredient of microbial preparation) such preparations include the fillers, stabilizers, stickers. The microbial insecticides on the base of *Bac. thuringiensis* are the most widespread. The biopreparation bitoxibacilline, manufactured by Ukrainian biolaboratories, contains the spore of microorganisms as a working ingredient as well as water-insoluble crystals of endotoxins and water-soluble thermo-stable crystals of exotoxins.

Bac. thuringiensis and its toxins have the intestinal effect on insects-pests. It is caused by processing of the plants with working compounds of biopreparation. The toxic crystals cause the paralysis of intestine getting into it together with fodder. As a result of this the intensity of nourishment is lowered, and hereinafter death of pests takes place. The first instance shows, that the larvae (caterpillars) perishes of poisoning by toxins or from reproduction of *Bac. Thuringiensis*, which causes the disease. The paresis of intestine is characteristic only for insects or its larvae, which have alkaline intestine contents meanwhile in acid solution these properties do not realize.

The pests, which did not perish of bacteriosis at larvae (caterpillars) stage, because of the insufficient for rapid death dose of preparations, struck in phase of chrysalis. At small preparation doses lowering of females' fertility and death of a number of larvae of consequent generation is frequently observed. The exotoxin causes the appearance of underdeveloped, misshapen and lacking vitality individuals.

The Ukrainian biolaboratories make effective microbial rodenticide preparation on the base of bacterium *satschenko* {*Salmonella enteritidis* var. *ratin*, v. *isatschenko*). The bacterium causes an epizooty of separate

species of mouse-like rodents. The protection from these pests plays an important role in increasing of harvest and it has an anti-epidemic significance, so the mouse-like rodents are the bearers and spreaders of dangerous for people and domestic animal infectious illnesses (tularemia, brucellosis, plague, foot-and-mouth disease, salmonellosis, pasterellosis, erizipeloides, pseudo tuberculosis etc.).

The preparations, created on the base of microorganisms really existing in nature, are not the means of annihilation, but the means of regulation of quantity of pests (that is reduction to economically not dangerous level). It is the important peculiarity of biopreparations in contrast to chemical pesticides, destined for extermination of harmful organisms.

Besides, the application of microbial preparations is accompanied with rise of quantity of useful fauna and stabilization of biocenological relationships in ecosystem. This is its main ecological advantage. It becomes especially noticeable during many years usage of biopreparations on the same fields of many years cultures.

The ecological advantage of microbiological means in comparison with chemical ones is also its high specificity in respect to definite species of harmful organisms and natural mechanisms of disintegration of microorganisms, which has developed in process of evolutions. At the same time the synthetic pesticides are the strange combination for nature. All this advantages allow suggesting, that biological method is ecologically clean.

For successful rational and economical use of microbial means funds of plants protection against pests and illnesses, the tactics of use of such means must differ from chemical pesticides, because the application of them by analogy with chemical pesticides is scanty and reduces the possibilities of

Num-ber	CHEMICAL PESTICIDES	BIOPREPARATIONS
11	High toxicity of wide action spectrum	Limited term of application
22	Toxic for people and for unpurposed organisms	The special conditions of application and storage of biopreparation are required
33	Remote effects of action (embriotoxicity, teratogenicity, gonadotoxicity, mutagenicity, cancerogenecity)	
44	Ability to accumulate in organism	
55	Break of natural biocenosis	
66	Relative stability in environment	
77	Ability to accumulate in environment	
88	The special clearance methods from pesticides are required	
99	Lowering of soil fertility	
10	Relatively high cost of pesticides production	

Table 2. Comparative list of disadvantages of biopreparations and chemical pesticides

microbiological pest control. Biopreparations act more slowly than chemical pesticides. So, it should be taken into account, that the main and important peculiarity of microbial insecticides is their strong influence on nourishment activity of pests. The peculiarity of action of microbial rodenticide is the beginnings of epizooty among rodents. The pests dye more slowly.

On the base of numerous experimental and natural researches concerning toxicology-hygienic study of industrial microorganisms and microbial preparations, used for plants protection, we worked out the principles and methods of potential danger estimation of biotechnology products on the base of natural strains of microorganisms. The methodical requirements were prepared. Methodology provides the successful study of pathogenic features of strains of microorganisms and marketable forms of biopreparations on this base [1].

Later these elaborations formed the basis of other methodical documents worked out with our participation. These documents concerned the methods of safety estimation of wider circle of biotechnological products and natural microorganisms-producers.

The results of our long term research concerning studying of safety of natural strains of microorganisms (*Bac. thuringiensis*, *Bac. subtilis*, *Bac. polymyxa*, *Pseudomonas carnea*, *P. aureofaciens*, *P. fluorescens*, *P. mycophaga*, *P. aurantiaca*, *Azospirillum brasilensis*, *Achromobacter album*, *Agrobacterium radiobacter*, *Beauveria bassiana*, *Trichoderma lignorum* and oth.), along with data of many other researches from different countries testify that entomopathogenes microorganisms, antagonists of plants pathogens, the microorganisms - producers of regulators of plants growth -are not infective for non-purposing organisms of all categories. In many cases it was difficult to define a virulence dose, because the death of animals dur-

ing the introduction of microorganisms into laboratory in maximum possible doses was not observed [1].

At present there are sufficiently numerous, although fragmentary, materials testifying about non-toxicity of marketable forms of biopreparations for diverse classes of non-purposing animals - fishes, useful insects, birds, mammals, including primacies and human.

At the same time a number of strains and biopreparations when entering into organism in big amounts (by air, contaminated by microorganisms) can cause allergenic effect, disbiotical changes of normal microflora of organism, can irritate the mucous membranes, for example, conjunctive. It should be noticed that high air contamination can be observed in the areas of industrial production of biopreparations in conditions of the non-maintenance of technology or non-perfection of technological equipment.

Because of possible unfavorable action of biopreparations the national local bodies on registration of such preparations, and international organizations WHO and FAO recommend to carry out the study of effectiveness and economy of such preparations and to assure their safety for man and environment.

Summarizing own research data along with data of Ukrainian and foreign authors we have worked out the national requirements. These requirements are used by the Ministry of Ecology and Ministry of Public Health (its Hygienic regulation Committee) during process of of biopreparations registration.

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A HEXACHLOROCYCLOHEXANE-POLLUTED SITE IN ALBANIA, ENVIRONMENTAL AND HUMAN HEALTH PERSPECTIVE

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INTRODUCTION

The post-communism political-social events during the 1990s in Albania were - besides many positive aspects - characterised by a 'misunderstanding' of the concept of freedom. In the context of this 'freedom' and due to lack of state control, many enterprises and other constructions, such as depots of pesticides belonging to former agricultural cooperatives, were destroyed. This uncontrolled phenomenon had important impacts on the environment.



The Lindane Plant-Porto Romano, part of a Chemical Plant, was located in Porto-Romano, ca. 6 km from Durrësi city (Albania), not far from the Adriatic Sea. Till the early 1990s, when it was still in operation, it has been a source of pollution because of low-level technology and the mishandling of technological residues. The problem of pollution was aggravated severely during 1991-1992, when the plant was destroyed and all the technological residues, mostly technical hexachlorocyclohexane (HCH), but also other chemicals, were left outside. In 1998 there were about 250 tons of residues of technical HCH, packed in about 10,000 very damaged sacks.

In September 1998 the biggest part of the technological remains was repacked and removed to a depot belonging to the same chemical enterprise, but the area is still highly contaminated due to a long-term soil contamination as well as many residues of building material originating from the destroyed plant. These materials have again been used as construction material for housing in the contaminated area during the 1990s. In fact, the site of the former Lindane plant

is of most immediate concern regarding environmental pollution and long-range transboundary air pollution. Several thousand people living in the near surroundings of the plant, some families residing within its territory in the half-destroyed buildings, children playing on the contaminated soil - these facts make concerns about the pollution even more serious in the perspective of human health impacts.

The former Chemical Plant Durrës is identified from a UNEP Post Conflict Environmental Assessment and State of the Environment Report in 2000 as one out of five environmental 'hot-spots' in Albania. The area is considered to be one of the worst environmental hot-spots in the Balkans¹.

HEXACHLOROCYCLOHEXANE ISOMERS, DIFFERENT BEHAVIOUR AND EFFECTS ON ORGANISMS

Belonging to the same chemical species, the HCH isomers have different physical, chemical and biological properties. The toxicity of each of the five isomers of HCH differs. Gamma-HCH (lindane) has the most expressed acute toxic effect on mammals compared to the other HCH-isomers. It is also the only HCH isomer with insecticidal properties. On the other hand, beta-HCH is stored most readily and for the longest time in the body fat and is therefore more likely to produce chronic toxicity at much lower levels of feeding. beta-HCH is the predominant HCH isomer accumulating in human tissues. Beta-HCH concentrations in adipose tissues are higher than those of other HCH isomers - a phenomenon that reflects the greater accumulative properties of beta-HCH. Reported concentrations in blood, serum and plasma varied between different countries and ranged up to 25 ug/litre³.

Numerous studies have demonstrated hepatic, neurotoxic, reproductive, developmental and immunotoxic effects of Lindane on animals. Renal dysfunction was observed in male rats in different studies⁵.

In humans, the most commonly reported effects associated with oral exposure to gamma-HCH are neurological. The evaluation of the effects of the other HCH isomers to humans is considered difficult, if not impossible, as it derives from the exposure to the technical HCH, which is a mixture of the HCH isomers⁵.

International Agency for Research on Cancer (IARC, 1987) evaluated the HCHs and concluded that for the technical grade and alpha-isomer there is sufficient evidence for carcinogenicity to animals. The HCHs are classified in group 2B: possibly carcinogenic to humans. Certain HCHs cause central nervous system, reproductive and endocrine damage.

The potential adverse effects of alpha- and beta-HCH on humans cannot be balanced against benefits, since these isomers have no insecticidal action. Their presence in the environment is thus of serious concern⁴.

ASSESSMENT OF POLLUTION IN DIFFERENT ENVIRONMENTAL COMPARTMENTS IN PORTO-ROMANO

Considering the high relevance of the region concerning environmental and human health, different studies and surveys have been carried out during the period 1999 - to date,

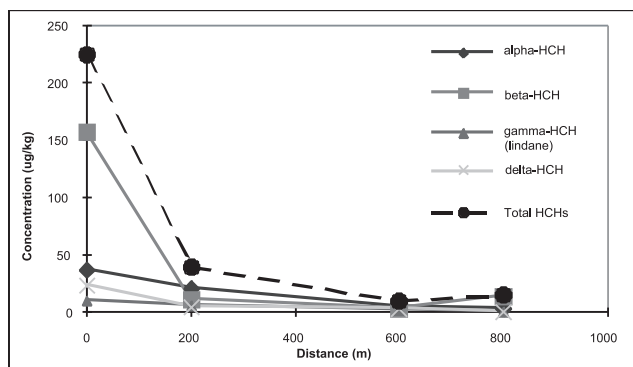


Figure 1: Concentrations of HCHs in soil (ug/kg dry matter) as function of the distance from the former Lindane Plant

in order to evaluate the level and expansion of the pollution. In this frame, the following environmental components were taken into account:

Soil/sediments: In order to assess the longitudinal propagation of the pollution in soil and in sediments of drainage canals, lying nearby the former Lindane Plant, soil and sediment samples have been taken in 1999⁷. Considering two determinants, that both favour the propagation of the pollution in the direction West-East: the flow-direction of waters during heavy rains, and the dominating direction of the wind, a transect sampling pattern⁸ was chosen along this direction. Soil and sediment samples from drainage canals were taken at 200m intervals. Top layer soil samples were taken, after removing any casual vegetation (depth 0-10 cm).

The analytical results for the evaluation of the *longitudinal expansion of the soil pollution* are presented in Fig.1. The low mobility of beta-HCH explains the swift decrease of its concentration with the distance from the source of pollution, in comparison to the other isomers of HCH. The finding of high levels of beta-HCH at the territory of the former Lindane Factory is indicative of local technical HCH contamination⁶.

One significant point to be noticed in the graphic is the distance of 200 m, where there is an obvious and significant decrease of the concentration of total-HCH from 226.8 ug/kg dry matter in the territory of the Lindane Plant to 42.7ug/kg dry matter. Nevertheless, from Figure 1 it can be seen that even at a distance of ca. 800 m, the sum of the hexachlorocyclohexane isomers is yet relatively high, namely 14.17 ug/kg dry matter.

The results of the analysis of the *sediment samples* taken from drainage canals at the area near the former Lindane Plant are presented in Figure 3⁷. This figure shows a decrease in the level of contamination from total-HCHs with the distance. So, while the total HCHs are found in very high levels in the sediments of the drainage canal next to the Lindane Plant (1878 ug/kg dry matter), the concentrations fall drastically with the distance. In similarity to the soils, this can be explained with the low mobility of HCHs. Furthermore, sediments usually contain more organic matter than soil, helping the adsorption of HCHs, which explains also much higher HCH levels in sediments, compared to soil.

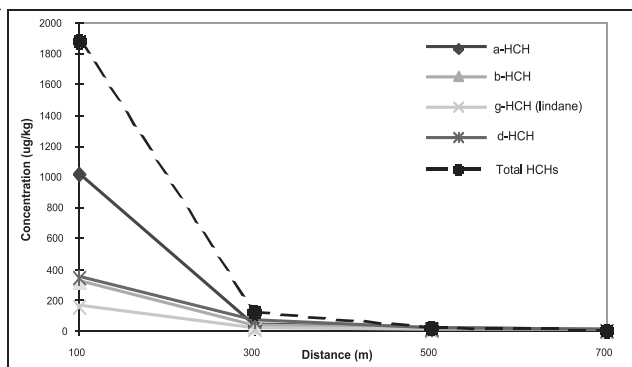


Figure 2: Concentrations of HCHs in sediments (ug/kg dry matter) as function of the distance from the former Lindane Plant

Sediment samples were also taken at a water stream, where all the waters from the area are drained during the rain season. This stream flows ca. 900m from the former Lindane Plant and is discharged to the sea, ca.3 km from the former plant. A sample taken along the above-mentioned sampling axis contained 41.5 ug/kg total HCHs.

The concentrations found in a sediment sample taken before the discharge to the sea were even higher (225.7 ug/kg dry matter total HCHs). Those results indicate a transport of the pollution towards the sea through erosion of the finer fractions of soil, which have, apart from a higher mobility, the property to adsorb the pollutants⁷.

The levels of HCHs found in sediments in the vicinity of the territory of the former Lindane Plant are ca. 2 times higher than the critical value for further investigations in the framework of soil sanitation, i.e. 1 mg total of organochlorine compounds /kg soil⁹.

In order to evaluate the *depth of the penetration of pollutants into the soil*, an earth profile (up to 80 cm, because of reaching concrete during sampling) was dug and 20cm depth fractions were taken⁷. The analytical results are presented in Figure 3. The higher found levels were those of beta- and alpha- HCH. Considering that the most persistent isomer of HCH in soil is beta-HCH, the high levels of the alpha-isomer can be explained by the greater initial content of alpha-isomer in the syntheses-mixture of hexachlorocyclohexane (65-70 % of the synthesis mixture)^{4,5}. The remainders deposited at the area of the former Lindane Plant were mostly technological residues of the Lindane production, i.e. a mixture of all the isomers of HCH.

Lower levels of alpha- and gamma -isomers in the first fraction (0-20 cm) than in the second one (20-40 cm) can be explained by biotic and abiotic degradation by UV irradiation in the surface⁴.

Studies have shown that in comparison with other HCH-isomers, the beta-HCH has the lower mobility in the flooding waters and does not move through the soil⁴. This low mobility of beta-HCH, together with the bigger persistence of the beta-HCH, can also explain the exponential pattern of the depth profile of beta-HCH in soil in our study.

According to RIKILT (1985), caution should already been taken with animal's grazing at levels as low as 50 ug beta-HCH per kg of soil. The Ministry of Agriculture and

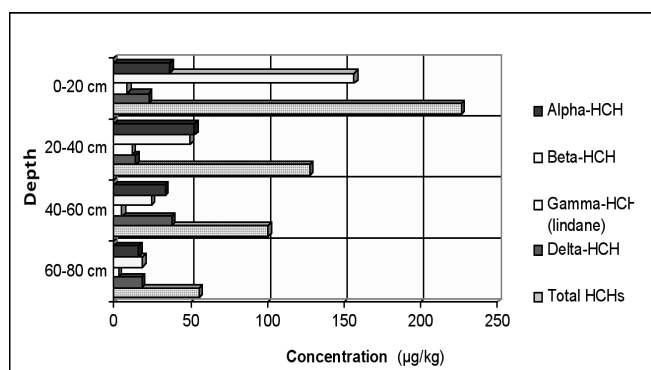


Figure 3: Depth profile of the content of HCHs in soil (ug/kg dry matter), area of the former Lindane Plant

Fisheries of the Netherlands (1986) applies signal values for substances hazardous to the environment, such as HCH, present in polluted soils. These values vary from 0.01 mg beta-HCH/kg dry substance for the grassland to 0.2 mg beta-HCH/kg for arable land. For horticultural land for flower cultivation, this chemical should not be present. In accordance with the Discussion Paper on Soil Quality (1986), for beta- and gamma-HCH a level of 10 ug/kg dry substance is considered a tentative reference value for multifunctional soil. For all combined halogenated hydrocarbons, a limit value of 20 ug/kg dry substance is being applied⁹.

The concentrations found in our study for beta- and total-HCHs in soil in the territory of the former Lindane Plant, respectively 156.8 and 226.8 ug/kg dry matter exceed respectively 16 and 11 times those tentative reference values for multifunctional soil. Considering that families are living in the territory of the former Lindane Plant and in its vicinity, the found levels of HCHs are very high for a long-term exposure. We could not find reference values for inhabited areas, probably because such a situation of living in an industrial contaminated area is very specific.

An apparently similar situation of pollution from HCHs has happened in different locations in the Netherlands, as result of their manufacture during the 1950s (spillage during production, storage and handling). Concentrations up to a few grams of HCHs/kg dry soil have been found. Further pollution has been caused by the dumping of chemical waste and its use in the levelling of certain areas 4, 5.

Soil samples taken in the territory of Lindane Plant from a UNEP environmental assessment mission showed extremely high HCH-isomer concentrations, in the range of 1,290 mg/kg to 3,140 mg/kg¹.

Water: One water sample was taken from a well at the territory of the former Lindane Plant, as well as two surface water samples, one from the main water stream along the sampling axis and the other before of discharge to the sea⁷. The results of the analyses of the *surface and groundwater samples* are presented in Table 1. After the European Council's Directive of 9 October 1984 on "limit values and quality objectives for discharges of hexachlorocyclohexane", the maximum recommended concentration of the total HCHs in inland surface waters is 50 ng/litre (0.05 ug/litre). In inland surface waters affected by discharges this concentra-

Compound	Water stream Sampling axis	Water stream, before discharge to the sea	Water, well in contaminated area
alpha-HCH	0.062	0.071	0.593
Beta-HCH	0.071	0.043	0.549
gamma-HCH (lindane)	0.07	0.062	0.1626
delta-HCH	0.078	0.075	0.1604
Total HCHs	0.28	0.25	1.47

Table 1: Concentrations of HCHs (in ug/litre) in surface and groundwater samples in the studied area (Porto-Romano)

tion must not exceed 100 ng/litre (0.1 ug/litre). As we see from Table 1, the results obtained for the surface waters were about five times higher than the concentrations recommended from the European Council for inland surface waters and more than two times higher than the maximum recommended concentration for inland waters affected by discharges¹⁰.

Comparing the levels of the concentrations of HCHs in surface waters in our study with those of the literature for different periods, they look comparable to the levels of the big rivers of Europe during the 1980s. In the review of the literature, it must be kept in mind that the decrease of the levels reported after 1975 is not only due to the restriction of the use of technical HCH at the beginning of the 1970s, but also the analytical technology, conditions and knowledge have continuously changed. So, it is important to separate the information from the literature¹¹.

The levels of HCHs in the groundwater are about three times higher than the maximum residue limit for pesticides in drinking water (EC) that is 0.5 ug/litre for the sum of pesticides. Those levels are also more than 3 times as high as the critical value for further investigations for groundwater, that is 0.5 ug/litre⁹.

Recent research has shown that HCH can degrade to the intermediates monochloro-benzene and benzene. Samples taken by UNEP1 confirm the obvious degradation of the site. A groundwater sample from a water well showed 4.4 mg/litre of chlorobenzene, over 4,000 times the acceptable level for drinking water in some EU nations. Repeated exposures to large quantities of chlorobenzene can adversely affect the nervous system, bone marrow, liver, kidneys, blood and reproductive organs. The measured concentrations of HCH-isomers in water samples were comparable in both above-mentioned surveys.

A **milk sample** showed a HCH content of 4.86 mg/kg of alpha-HCH, 7.27 mg/kg of beta-HCH, 0.13 mg/kg of gamma-HCH, 0.47 mg/kg of delta-HCH, and 0.084 mg/kg of epsilon-HCH. These levels are 40 times the German trigger level for alpha-HCH (0.1 mg/kg) and 100 times the trigger level for beta-HCH (0.075 mg/kg)¹.

The found concentrations suggest that the milk cannot be used for human nutrition without posing a serious health risk. It can be assumed that the concentration of HCH-isomers in the animal's tissue is much higher¹.

Subject No.	Gender	Age (years)	Position of residence	Duration of residence* (years)	Number of children, age*, **
1	Male	60	Territory of Factory	3	
2	Female	30	Territory of Factory	3	1 (1.5 years old)
3	Male	23	Territory of Factory	3	
4	Female	25	• 100 m North of the Factory • • Territory of Factory	2 1	1 (5.5 years old)
5	Female	48	120 m north of Factory	2.5	4 (adults)
6	Female, daughter of subject No. 5	20	120 m north of Factory	2.5	–
7	Female***	30	Tirana		
8	Female***	25	Tirana		

* Applicable for the subjects living in the territory of the Lindane Plant in its vicinity.

** Applicable for female subjects.

*** Control group

Table 2: Data on the subjects (blood samples)

Subject No.	alpha-HCH	beta-HCH	gamma-HCH	delta-HCH	Total HCHs
1	2.9	81.5	n.d.	n.d.	84.4
2	1.6	5.5	0.5	n.d.	7.6
3	2.2	25.1	n.d.	n.d.	27.3
4	2.3	91.5	n.d.	n.d.	93.8
5	n.d.	1.4	n.d.	n.d.	1.4
6	n.d.	0.5	n.d.	n.d.	0.5
7	n.d.	n.d.	n.d.	n.d.	0.0
8	n.d.	n.d.	n.d.	n.d.	0.0

Table 3: HCH isomers concentrations in blood (serum) in ug/L

The presence of HCHs has been determined in a number of important food items in France by Laugel (1981). In milk and milk products (2688 samples) the average level was 0.05mg/kg alpha-HCH (ranging from undetectable to 0.22 mg/kg), 0.03 mg/kg beta-HCH (n.d. to 0.25 mg/kg). A study from Hildebrandt et al. (1986), for the years 1973-1978 reports for milk and milk product samples from The Federal Republic of Germany a maximum level of 0.015 mg/kg alpha-HCH and 0.05 mg/kg beta-HCH (on a fat basis). The levels are ranging from 0.01-0.03 mg/kg alpha-HCH and <0.01mg/kg beta-HCH (on a fat basis) for the years 1979-1983.

In a total diet study in the United Kingdom, 24 samples of each food group were analysed for HCHs. For milk, there was found for alpha-HCH a mean value of 0.0005 mg/kg (n.d.-0.002 mg/kg) and for dairy products, a mean of 0.006 (n.d.-0.02 mg/kg product). For beta-HCH the values were < 0.0005 (n.d.-0.001) mg/kg for milk and 0.001 (n.d.-0.008) mg/kg in dairy products (HMSO, 1986)⁴.

The Maximum Residue Level (MRL) of lindane in milk was 10 ug/kg in 1984 ¹³, while we could not find MRLs for the other HCH isomers. The concentration in our milk sample was higher than MRL.

As an effort to evaluate the exposure of the population living in the contaminated area, blood samples were taken in 2002 from volunteers of different age and gender, living in the territory of the former Lindane Plant and in a distance approx. 120 m to the north of the factory ¹⁴. Two samples were taken from two subjects in the Maternity Ward of Tirana as control.

As the history of a subject is very important when considering HCHs levels in blood, we have presented some personal data at the time of exposure of the subjects in Table 2, whereas the analytical results for the levels of HCHs in blood (serum) are presented in Table 3.

The analytical results clearly show a dominance of the beta- HCH, comparing to other HCH-isomers. The presence of high levels of beta-isomer of HCH compared to other HCH-isomers can be explained with the capability of this isomer to accumulate and persist longer than the others.

The levels of HCH-isomers dropped significantly with the distance from the factory, to very low levels for subjects living in a distance of 120 m to the north of the factory. The predominating direction of the wind and of the water flowing during heavy rains, i.e. West-East, can have influenced this drop.

In literature a tendency is described of the decrease of HCHs levels in blood with the age after 50 years, which was also observed during the comparison of the HCHs levels in the serum of subject 1 (60 years old, total HCHs 84.4 ug/L) and subject 4 (25 years old, total HCHs 93.8 ug/L), both with similar exposure time. These values are obviously exceeding the reference values for lindane for various exposures (INERIS), i.e. 20-25 ug/L¹⁵.

The lower levels of HCHs in the blood of subject 3, 30 years old, with a similar exposure time with subjects 1 and 4, could be related to the diminishing of body burden, due to her delivery / breast feeding, as she has a 1.5 year old child.

The relative weight of beta-HCH to total HCHs concentrations in serum was 74-97 %.

These preliminary data evidence the necessity for more extensive studies in this contaminated area and of measurements required for the protection of human health and the remediation of the environmental situation of the region.

CONCLUSIONS/RECOMMENDATIONS

1. The area of Porto-Romano, Durres is contaminated from HCH-isomers as result of the production of lindane and of mishandling of the technological residues. The levels of HCHs in the territory of the former Lindane Plant exceed tens times the tentative reference values for a multifunctional soil.

2. The pollution of the soil from HCHs in the field in

front of the former Lindane Plant has an exponential model, with an important decrease of the levels of HCHs after a distance of 200m. The concentrations of HCHs found in the sediments near the territory of the former Lindane Plant are ca. 2 times higher than the critical value for further investigations in the framework of soil sanitation.

3. The surface waters seem to be affected from the contamination of the region. In spite of the low mobility of the HCHs, their level in the groundwater under the territory of the former Factory is higher than the critical value for further investigations of groundwater.

4. The found concentrations of HCHs in milk suggest that the milk cannot be used for human nutrition without posing a serious health risk. It can be assumed that the concentration of HCH-isomers in the animal tissue is much higher.

5. Very high levels of beta-HCH were found in the blood of persons, which confirms a high, continuous exposure of the population living in the territory of the former Lindane Plant and its surroundings.

6. Several thousand people living in this area, as well as expansion and transport of the chemicals towards the sea, make the concern about the pollution even more serious. It is necessary to resettle the citizens living in or near the polluted sites in order to minimise the negative health effects.

7. Further efforts to assess and monitor population health risks as well as sanitation/ monitoring of the area are needed.

In order to handle the environmental pollution situation, strengthening of national institutions dealing with environmental problems is a challenge that Albania is meeting and will hopefully cope with in the near future, with a constructive support from international organisations.

THE OBSOLETE PESTICIDES STOCKS IN BULGARIA – A SOURCE OF LONG-TERM CONTAMINATION OF THE ENVIRONMENT

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ABSTRACT

The stocks of obsolete pesticides are point sources of pollution and representing a risk for soil and groundwater contamination. Monitoring studies were carried out aiming to determine the concentrations and distribution patterns of pesticide residues in soil around the formulations depots or places where formulations were buried.

INTRODUCTION

The problem with the presence of huge amounts of obsolete pesticides in great number of depots in Bulgaria has

been a source of concern and has been handled by national authorities (Ministry of Agriculture, commissions on protection against disasters etc.) for more than 10 years. Since that time, collection the formulations in central depots or burying in concrete cubes were undertaken although a great number of storage places still not corresponding to safety requirements (Ministry of Agriculture and Forestry, personal information). Often the storehouses were not designed and equipped adequately to prevent pollution of the surroundings. Cases of wells and groundwater contamination occurred as a result of formulations spilling due to damaged packing or burying pesticides in soil.

The elimination activities of the obsolete pesticides collected in the storehouses are directed to solve only one face of the problem, which concern the ecological consequences of the presence of unwanted chemicals. Chemicals released at high concentration rates in soil considered as a source of long-term and boundless potential hazard for environmental pollution. Such point sources of extremely high concentrations of toxicants in soils are represented by pesticide formulations depots, the places for preparation of working solutions and rinsing sprayers, waste disposal places, storage

places of banned or unwanted pesticides, etc. The point sources of high pesticide concentrations are considered to be responsible to a greater extent for the groundwater pollution compared to the pollution resulted from the normal field applications at the recommended rates (Roberts, 1990, Helveg, 1993a, Stobiecki and Pruszyński, 1995). It is confirmed that the behavior of pesticides in the soil environment is influenced by the concentration rates. According to Helveg, 1993a; Mayka *et al.*; 1992a; Rao and Davideps, 1994, the leaching rates in soil profiles increase under extreme concentrations due to a surpass of the soil sorption capacity. Chemicals leached to the subsurface soil layers represent a high risk for groundwater pollution because of the low organic matter content which results in low sorption capacity (Helveg, 1994). A crucial factor responsible for increasing the environmental risk of pesticides under high concentration conditions is the fact that the degradation rates of xenobiotics decreases significantly at higher concentrations in soil (Mayka, 1992b; Helveg, 1993b). Pesticides half-lives in subsoil are found to be 5 to 20 times longer than in surface soil (Helveg, 1994; Fomsgaard and Helveg, 1993).

During the present study, the following presumptions were taken into consideration:

1-Huge amounts of toxic substances were present in the open areas around the pesticides depots;

2-These compounds underwent vertical and horizontal migration in soils;

3-They could be subjected to leaching into groundwater, evaporation to the atmosphere, absorption in crops etc.; thus the study aimed to monitor the real situation and to assess the potential risk for environmental pollution caused by the point sources of pesticides.

METHODOLOGY

Two years (1994 - 1996) observations were carried out on pesticides pollution in the neighborhood of selected representative sites in Sofia district: The selected sites included 6 storehouses of pesticide formulations (Kostinbrod, Aldomirovtsi, Vakarel, Bojurishte, Ichtiman) and one site for preparation of working solutions of agricultural aviation (Slivnitsa). All these sites have not been in use for about 5-6 years. Another site where unwanted pesticides were buried was also observed 10 years after the removal of the chemicals (village Zlatusha). Samples were collected from plots in front of the depots and at 50 m distance. Soil drill was used for sampling until 1 m depth at 20 cm layer interval. Individual samples were collected from 10 points at each plot of the selected layers and after homogenization, laboratory samples 1 kg each were taken. Information was collected on the pesticide formulations stored in the depots. 27 target pesticides belonging to 9 groups including organophosphorus (OP) (dimethoate, chlorpyrifos, chlorpyrifos-methyl, fenitrothion, parathion-methyl, phosalone); organochlorine (OC) (lindane, endosulfan, heptachlor, p, p'-DDT, o, p-DDT, p, p'-DDE, o, p'-DDE); triazines (atrazine, simazine, metribuzine); dinitroanilines (trifluralin, pendimethalin); acetamides (alachlor, acetochlor, metolachlor); phenoxycarboxilic acids (2,4-D, MCPA); benzoic acids (dicamba);

phenylureas (linuron, diuron) and nitrophenyl ethers (nitrofen) were selected according to the information obtained.

Gas chromatographic (GC) method (Balinova and Balinov, 1991) was used for determination of OP, OC, dinitroanilines, acetamides while high performance liquid chromatographic (HPLC) method was used for phenoxycarboxilic acids, benzoic acids, phenylureas (Balinova, 1993). Both GC and HPLC were used for the determination of triazines in order to confirm the identification. The identification of the pesticides of the other groups was confirmed using two chromatographic columns of different polarity.

RESULTS AND DISCUSSION

In all cases, soils in the neighborhood of the observed point sources were heavily polluted with complex of different pesticides. 14 of the target compounds were determined in the surface soil samples with different frequency of occurrence and concentrations as shown in Table 1.

Pesticide	Frequency %	Maximum concentrations (mg/kg)
2,4-D	100	783
p,p'-DDE	85.7	29.4
p,p'-DDT	71.5	700
o,p-DDT	71.5	200
Atrazine	57.2	18.9
Fenitrothion	50	32.8
Pendimethalin	50	99.2
Dicamba	50	128.9
Alachlor	33.3	76.9
Metolachlor	33.3	1.8
Simazine	28.6	1.5
Trifluralin	16.7	34545.5
Linuron	16.7	2.5
Nitrofen	14.3	40

Table 1: Frequency of Occurrence and Maximal Concentrations of Pesticides in the Surface Soil

Extremely high concentrations were determined for some compounds such as trifluralin, 2,4-D and p, p'-DDT in the surface soil that were thousands times exceeding the concentrations resulting after normal agricultural practice.

Herbicides were determined with high concentrations and frequencies. 2,4-D was detected at all the observed sites. This corresponds to the great quantities of this particular group used in agriculture for decades preceding the study.

DDT (isomers and metabolites) was only detected complex of the organochlorine pesticides group. These compounds were practically detected in all samples. Lindane was detected at very low concentrations.

The extremely high concentrations of pesticides detected in the surface soils pose the necessity to study the

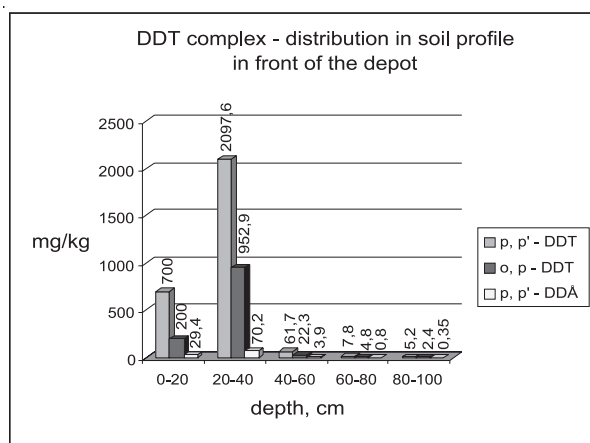


Figure 1:

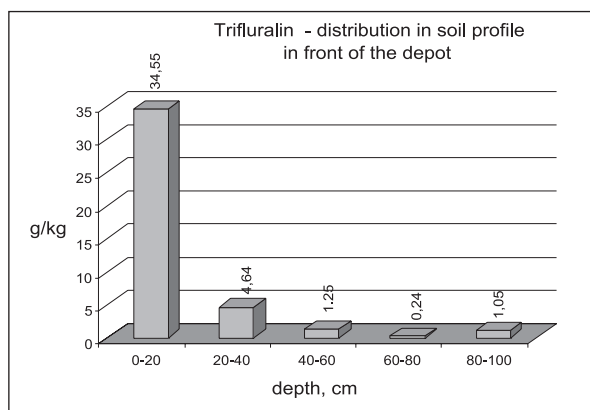
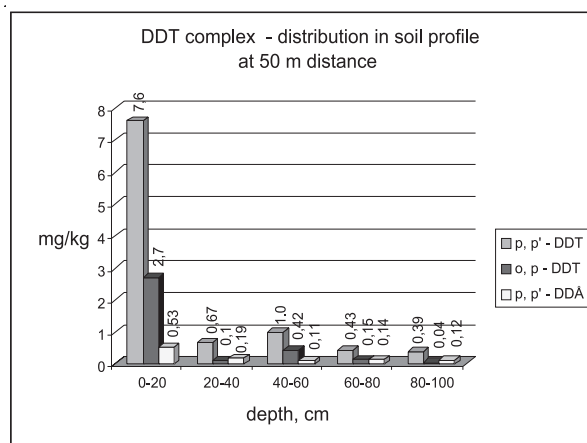


Figure 2:

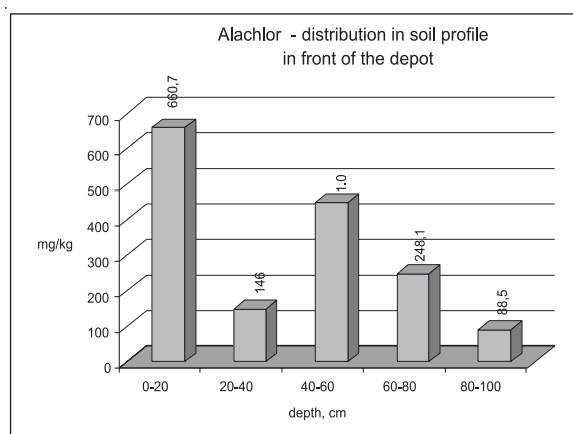
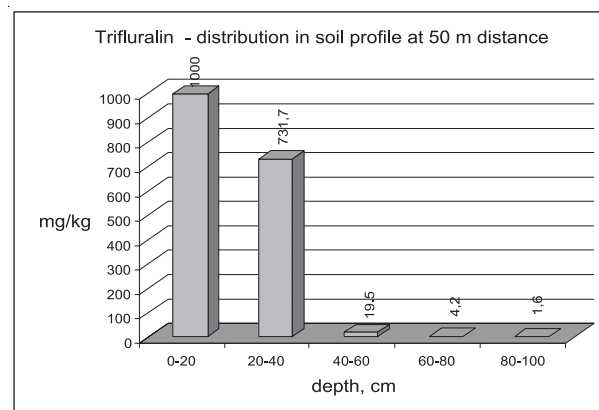
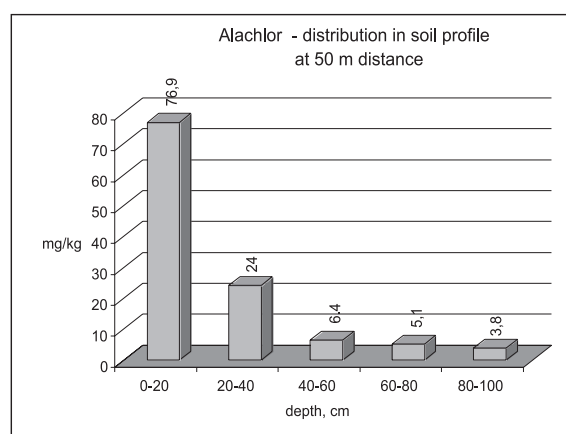


Figure 3:



influence of this factor on their behavior in soil and particularly their leaching into soil profile and their persistence in subsurface soils.

Characteristic examples of distribution patterns of the selected pesticides in soil profiles are shown in Figures 1 – 4.

Results confirmed that the rate of the vertical migration of the investigated pesticides into soil profile is strongly influenced by their concentrations. Compounds characterized as nearly immobile in soil, such as DDT and trifluralin (Hafner, 1994), showed remarkable leachability under conditions of permanent extreme concentrations. Residues within a range of about 1–5 mg/kg were determined at 80–100 cm depth. Some herbicides of high migration potential, such as alachlor and 2,4-D, were detected in the subsurface

layers at higher concentrations than in the surface soil (Figures 3 and 4). Maximum concentrations of 2,4-D were detected in soil layer at 60–80 cm depth.

The long-term inputs of high quantities of pesticides in the soil of the areas around the pesticides depots allow the toxicants to drain off to the subsurface layers irrespective the chemical structure and properties of the compounds. Leaching of the chemicals down to 1 m depth under conditions of extremely high concentrations is an indication of increasing the potential risk for groundwater pollution. These data confirmed the concept that the depots of obsolete pesticides represent point sources of soil and groundwater pollution.

Horizontal migration induced by water and wind erosion was also observed. Contamination at 50 m distance (Figures

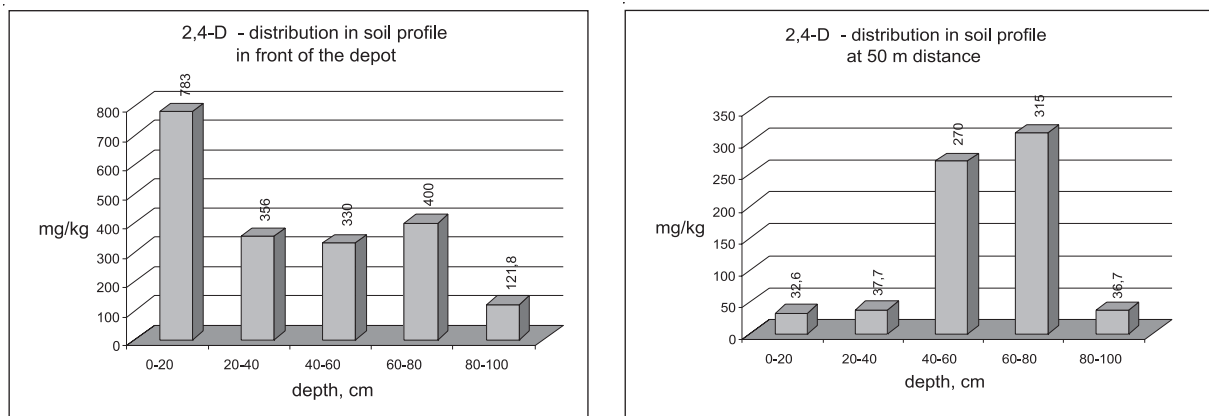


Figure 4:

1-4) was detected in most cases at similar rates as in vicinity of the depots indicating that a real hazard exists for the surface waters and groundwater, agricultural land, crops etc.

The contamination of the investigated sites was mostly a result of accidental events such as spilling of formulations, working solutions etc. The distribution of pesticides in soils was irregular. The occurrence of high residues at least 5 years after the last practices was due to the improper handling and the high rates of concentrations, which influenced the behavior patterns in soil environment. The half-lives of some active substances detected under conditions of normal agricultural practice and recommended rates of application were drastically exceeded. This fact was shown by the cases of long-term occurrences of non-persistent herbicides such as 2,4-D and alachlor at high concentrations in the soil profiles. The half-lives of these compounds in the soil ranged between 0.3 and 30 days for 2,4-D and 14 – 20 days (Khan, 1980). The increased persistence under conditions of extremely high concentrations in the soil confirmed the high risk for pesticides pollution from these point sources.

The phenomena of increased mobility and persistence of pesticides in soil induced by extreme concentration rates could be a result of the sorption capacity surpasses and destruction of the microbial activity in soils. A more detailed and precise explanation of these phenomena needs careful and extensive research. That was not in the scope of the investigation described.

The obtained results showed the current status of the environment near the pesticide formulations storehouses. Huge

amounts of toxic compounds were spread out in the open air. Soils around these storehouses were heavily polluted by complex of chemicals of high biological activity. Under the conditions of extremely high concentrations a significant increase of persistence and leaching potential was observed. The possibilities of migration to deep soil layers, surroundings, ground and surface water were demonstrated.

Pesticides detected outside the storehouses represent high potential risk of environmental pollution. The collection and removal of the formulations from the storehouses do not solve the problem with the active substances found outside. Development of adequate methodology and technology for detoxification of pesticide residues around the depots is mandatory. The methods should be environmentally friendly, effective and specific in dependence of the properties of pollutants and economically acceptable.

CONCLUSIONS

The soils around the depots of obsolete or banned pesticides, waste disposals and unwanted formulation storage places are point sources of extremely high concentrations of toxic chemicals.

They represent long-term and boundless potential hazards for environmental pollution. Monitoring of the existing point sources, determination of the concentrations and chemical structures of the pollutants are prerequisites for development of adequate and effective measures of detoxification for guarantee of environmental safety.

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OBSOLETE PESTICIDES IN ESTONIA

Ott Roots

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Policy in the area of “environment and health” must be oriented to the central idea of sustainable development, which harmonises economic activity and living with the natural bases for life and thus provides a decisive basis for making health possible for all.

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.

In Estonia the use of plant protection products enlarged in the end of 50-ies. In 1957 226t of pesticides were used, mainly DDT and hexachloran and in a less degree also seed dressing products. In 1959 it was started to use herbicides (Müür, 1996). The account of nomenclature and quality of using pesticides has been kept since 1960 (Annex 1- use of the plant protection compounds in Estonia in 1960-1992).

According to the Order from 21.10.1967 approved by the Government the import of chlororganic plant protection products were banned in Estonia (Müür, 1996). One can bring into Estonia and use only these pesticides, that are registered in the Estonian Republic (they don't include persistent organic pollutants – POPs). After Estonian independence in 1991, new regulations banned POPs a second time “Governmental Regulations: No. 6, 5 January 1999 on establishing a procedure for importing and exporting banned and strictly restricted chemicals and No. 36, 26 January 1999 on establishing the list of active substances banned to use in plant protection products (Dir 79/117/EEC).

In 1995, first attempts were made to register abandoned storehouses and to make an inventory of leftover pesticides. Preliminary evaluations showed that the amount of leftover and obsolete pesticides was nearly 300 tonnes, but by



recent studies the amount could be more than 500 tonnes with ca 130 individual pesticides recorded. The number of registered storehouses was 253. In 1996, the number of identified unsafe pesticide storage sites was about 1,500 in the three Baltic countries (900 in Lithuania and 400 in Latvia). Since 1996, programs have been carried out in all three countries to identify these pesticides, re-pack them and store them under safe conditions (2nd Baltic State of the Environment Report, 2000).

In 1997, a former military territory and storehouse in Paldiski were accommodated for temporary storage of old pesticides and military waste. The Ministry of Environment has initialised and organised the liquidation of abandoned pesticides. By the end of 1998 more than 400 tonnes of pesticides had been collected, repacked and stored in Paldiski storehouse for hazardous waste.

Pesticides are covered by the “Plant protection act” of 15 March 2000. Among other things the act contains a list of prohibited active substances in plant protection products, the procedure and methods for classification of plant protection products, and the requirements for packaging and labelling of plant protection products.

Today none of the POP pesticides are used in Estonia. The Plant Protection Inspectorate has provided information on which of the nine POP pesticides that have been imported and used in Estonia in recent years (Table 1).

Pesticide	Year of import ban	Use/No use	Comments
Aldrin	1968**	No	Never used or imported.
Chlordane	1968**	No	Never used or imported.
DDT	1968*	Yes	Last used in 1971. Amounts of obsolete DDT in stores 5,6 tonnes***
Dieldrin	1968**	No	Never used or imported.
Endrin	1968**	No	Never used or imported.
Heptachlor	1968**	No	Never used or imported
Hexachlorobenzene	1968**	No	Never used or imported.
Mirex	1968**	No	Never used or imported
Toxaphene	1968*	Yes	Used until 1984. All products were used. No stocks exist.

Sources: * - The Estonian Plant Protection Inspectorate, 2000. ** - Müür – 1996. ***-2nd Baltic State of the Environment Report, 2000.

Table 1: Past use of POP pesticides in Estonia (Status on POPs Phase-out in the Baltic States (Estonia), 2001)

Species	Location	Depth,m	Time	Age,year	Size,cm	Sex
Herring (12–15)	Open sea	n.s	Aug–Sept.	N/2+,3+	n.s	Female
Cod (12–15)	Open sea	n.s	Aug–Sept	S/1+,2+	24–35	Female
Macoma baltica 80g	Open sea	n.s	Sept	n.s	>0,5	n.s
Saduria ent. 80g	Open sea	n.s.	Oct–Nov	n.s	4–6	n.s.* *
Uria Aalge (10)eggs	Islands open sea		1–15 May	n.s.	n.s.	n.s.
Flounder (10–15)	Coast ***	<20	Aug–Sept	2+	n.s.	Female
Viviparous Blenny (10–15)	Coast***	<20	Nov–Dec	n.s.	17–30	Males****
Perch (10–15)	Coast	n.s.	Aug–Sept	n.s.	15–20	Females
Sterna hir. (10)eggs	Coast		June–July		n.s.	n.s.
Mytilus Edulis 80g	Coast	N/2–5 S/<15	Oct–Nov	n.s.	3–4	n.s.

* Manual for Marine Monitoring in the COMBINE Programme of HELCOM

** Eggs-carrying females avoided

*** Samples shall be collected away from river mouth

**** Males collected for chemical analysis before spawning (Aug), females collected in October for studies on reproductive outcome and fry development
S Southern Baltic, N Northern Baltic, n.s. not specified

Table 2: Overview of sampling requirements for contaminants *

In Vaivara a new landfill Vaivara Temporary Storage (Eastern part of Estonia – 30 km from Narva) for hazardous and non-hazardous waste was constructed in 2002. All the obsolete pesticides will have to be treated together since a large share of the stocks are unidentified or contains mixtures of chemicals. At the beginning of 2001, more than 110 tonnes of most dangerous obsolete pesticides were incinerated at the Ekokem incineration plant in Finland. In the 2003 Estonian Ministry of Environment will continue obsolete pesticides incineration. In Estonia we have stored today 486.4 tonnes of obsolete pesticides.

The main reason for analyzing toxic compounds from our surroundings (including food) is the need to determine how dangerous they are to people and their living environment. The comparison has so far been based upon the standards of the World Health Organization, but ever since the year 2000 we have been able to apply Estonian permissible limiting standards. On the 12th of January 2000 the Estonian Government passed a regulation number 14 “Enumeration of permitted pollution substances in food and enactment of limiting standards by food groups”.

It is thought that the people living near the Baltic Sea receive 80–85% of the total toxicants content namely from the fish. The contents of POPs in the Baltic Sea ecosystem have been studied in Estonia since the early seventies (Roots, 1996). Since 1994 the state monitoring carried out in Estonia has been funded from the state budget as ordered monitoring work (Estonian Environmental Monitoring, 1998).

Monitoring has been for a long time a well-established function of the HELCOM. Monitoring of physical, chemical and biological variables of the open sea started in 1979. Until 1992 monitoring of coastal waters was considered as a national obligation. The Environment Committee decided that for management reasons the different program should be integrated into a common structure and thus the Cooperative Monitoring in the Baltic marine Environment – COMBINE – was instituted in 1992 (Table 2).

Evaluation of bio-accumulation of toxic compounds into the organism of fish from Estonian coastal waters depending of their age, sex, maturity of gonads and fishing ground (Roots, 1996; 1999; 2001). Determination of changes in contents of toxic compounds, which are due to the nature of nutrition of fish. Comparing the results with corresponding indicators of the Baltic Sea countries and also with established standard norms, which will enable us to clarify how dangerous are the toxic compounds in fish to human health.

The selected bioindicator is, proceeding from recommendations of Helsinki Commission (HELCOM), female Baltic herring of two-three years of age. Samples of fish were collected along the Estonian coast at three sampling sites for baltic herring (*Clupea harengus*) and five sampling sites for perch (*Perca fluviatilis*). The fish were frozen promptly before examination and selection. Description of sampling techniques as well as the analytical procedures can be found on Roots (2001). Persistent Organic Pollutants (POPs) analysis took place in the Estonian Environmental Research

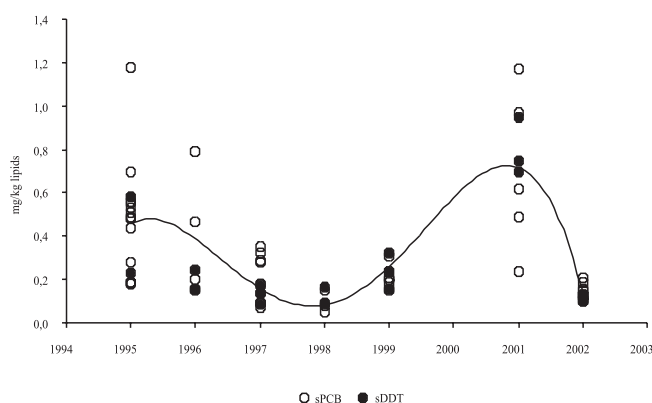


Figure 1: Contents of sDDT and sPCB (mg/kg lipids) in the muscle tissue of Baltic herring from different parts of the Estonian coastal sea (Roots and Simm, 2003).

Center. The Estonian Environmental Research Centre (EERC) is accredited by German accreditation bureau Deutsches Akkreditierungssystem Prüfwesen GmbH (DAP)(Reg. No DAP-PO3.131-00-97-01). EERC facilities are well-equipped, enabling precise determination of environmentally dangerous substances in different sample types.

Contents of dangerous substances in sea organisms have been studied in Estonia since the early seventies (Roots and Zitko, 2003). But earlier results (Roots, 1996) have only historical value, since the change in methods of chemical analysis – and especially the change in methods of analyzing organic substances – does not allow us to compare them with the latest results. This particular survey proceeds from the results obtained within the framework of the Estonian National Monitoring Program (“Monitoring of dangerous substances in the coastal sea”) and several other research programs.

The contents of organic compounds have been determined in the muscle tissue of Baltic herring and perch. Perch were caught during the years 1998–2001, from August to December. They were caught from the eastern part of the Gulf of Finland (Narva Bay), western part of the Gulf of Finland (near Dirham), Central Baltic (around Vilsandi island), Väinameri and Pärnu Bay. All together 99 perch samples were analyzed. Age of the fish varied between 1–11 years. Samples of 2–3-year-old female Baltic herring (all together 47 samples) were caught during the years 1994–2001 from the two areas in the Gulf of Finland (Tallinn and Kunda) and from the northeastern part of the Gulf of Riga (Pärnu Bay). The average content of chlororganic compounds in the muscle tissue of Baltic herring and perch does not differ significantly. The average concentration of DDT in the muscle tissue of Baltic herring and perch is 0,43 (SD – 0,05) and 0,53 (SD – 0,06) mg/kg per lipids, respectively (Roots and Simm, 2002). The average contents of DDT in herring and perch for the whole Baltic Sea vary between 0,061–0,71 and 0,071–1,0 mg/kg (Olsson et al., 2002). It may be concluded that the contents in fish from

the Estonian coastal waters do not significantly exceed the average indicators for the whole Baltic Sea. Somewhat higher determined maximum concentrations probably reflect the difference in the initial data – fish that we analyzed included substantially older fish (in case of perch, for example, some fish were 11 years old). Contents of DDT in the organisms of the Baltic Sea have been observed since the late sixties (Bignert, 1996). Concentrations of DDT have substantially decreased in most of the studied organisms, including Baltic herring (HELCOM, 2002). Concentrations of DDT in the muscle tissue of Baltic herring (caught from the Estonian coastal sea) were also considerably higher in the seventies than in the nineties (Roots, 1996, 1999). But the changes in methods of chemical analysis do not allow us to make a direct comparison between these results. Figure 1 shows that the concentrations of DDT in the muscle tissue of Baltic herring have decreased during the years 1994–1996 (Roots and Simm, 2003), but there is a certain rise after 1998. However, the reasons for this rise are not clear. We do not assume that large amounts of organic pollution substances have got into the sea environment during the last years. It can be assumed that the rise is caused by the deviation in the chemical analysis or – which is even more likely – in the representation of the analyzed samples.

Another reason may lie in the age difference of the analyzed herring – 3-year-old fish had a bigger part in the samples.

Concentrations of practically all the organic pollution substances are significantly higher in older than in younger fish. There is a statistically reliable connection between the age of the analyzed perch and the concentrations of DDT and PCB ($r^2 = 0,738$ and $r^2 = 0,680$)(Roots and Simm, 2002).

It can be concluded that the concentration of organic pollution substances in the muscle tissue of perch rises correspondingly to the age of the analyzed fish. Therefore, the data concerning 5–6-year-old perch from different parts of the Estonian coastal sea were used for comparing the concentrations of DDT. Both DDT and PCB concentrations in the muscle tissue of perch are considerably higher in the Narva Bay and Pärnu Bay than in other studied areas.

When considering the possible effects of consuming seafood, it is necessary to characterize communities and individuals according to the amounts they consume, since communities in different parts of the world are likely to show big differences in their consumption of seafood. For example, based on FAO food balance data, the European regional average consumption of seafood (fish and shellfish) is 60 g per person per day and in East Asia 79 g per person per day. The figure used to represent high consumption is 150 g per person per day (Reports and Studies, 1991).

The joint FAO/WHO Expert Committee on Food Additives (JECFA) generally sets the ADI (the acceptable daily intake) of a food additive on the basis of the highest “no-observed-effect” (NOEL) level in animal studies.

ADI is the daily dosage of a chemical which, during an entire lifetime, appears to be without appreciable risk on the basis of all the facts known at the time. Where an ADI

Vainameri Region 1997			
Perch	sum DDT*	3.0 x 10 ⁻³	part of ADI
(n=14)		0.3 x 10 ⁻³	part of NOEL
Length 10.3–11.4 cm	sum HCH	0.6 x 10 ⁻³	part of ADI
	sum PCB	4.0 x 10 ⁻³	part of NOEL
Vainameri Region 1999			
Perch	sum DDT	0.07 x 10 ⁻³	part of ADI
(n=10)		0.007 x 10 ⁻³	part of NOEL
Length 24.5–39.0 cm	sum HCH	0.9 x 10 ⁻³	part of ADI
	sum PCB	0.3 x 10 ⁻³	part of NOEL
Western coast of Estonia, Vilsandi National Park 1998			
Perch	sum DDT	0.2 x 10 ⁻³	part of ADI
(n=10)		0.01 x 10 ⁻³	part of NOEL
Length 19.2–27.2 cm	sum HCH	0.1 x 10 ⁻³	part of ADI
	sum PCB	1.0 x 10 ⁻³	part of NOEL
Flounder	sum DDT	3.0 x 10 ⁻³	part of ADI
(n=10)		0.2 x 10 ⁻³	part of NOEL
Length 19.1–28.8 cm	sum HCH	0.4 x 10 ⁻³	part of ADI
	sum PCB	0.8 x 10 ⁻³	part of NOEL

$sumDDT = p,p'DDE; p,p'DDD; p,p'DDT; sumHCH = \gamma\text{-HCH} + \alpha\text{-HCH};$
 $sumPCB = IUPAC \text{ No. 28, 31, 52, 101, 118, 153, 105, 138, 158, 163 and 180.}$

Table 3: Comparison with ADI and NOEL

has been established for a particular pollutant it will be noted whether the intake from seafood is likely to be a substantial part of the ADI (Reports and Studies, 1991). NOEL is the risk that may be incurred by especially susceptible groups, such as children and old people.

ADI and NOEL values used in our work are based upon the literature data (FAO/WHO, 1971, 1978, 1985; Reports and Studies, 1991).

DDT and its metabolites are some of the most frequently reported organochlorine contaminants in the environment. An overall NOEL for the toxicity of DDT of 0.25 mg kg⁻¹ body weight per day in humans and ADI of 0.02 mg kg⁻¹ body weight was set by the Joint Meeting on Pesticide Residues (JMPR) in 1984 (FAO/WHO, 1985; Reports and Studies, 1991). For example, if a person weighing 60 kg consumes 150 g d⁻¹ of fish containing 20 µg kg⁻¹ of DDT and its metabolites, the daily intake will be 0.05 µg kg⁻¹ body weight. This would constitute 1/400 of the ADI (Roots, 1996).

If we look at the amounts of toxicants obtained with food (fish), we can see that even the maximum levels of organochlorines found in the organism of Baltic fish (at the coastal areas of the Estonia) do not represent any human health risk, as they are lower than the standards set by the World Health Organization. Besides, our calculations were made on the ground of 150 g of edible fish per day, compared with the European average of 60 g per day (Roots, 1999). However, it is known that marine food is not the only route of human exposure and any overall risk assessment must take this into account (Roots, 1999).

It may be concluded that although the contents of chlororganic compounds in fish from the Estonian coastal waters do not exceed the average levels of the whole Baltic Sea, there are still clearly defined areas, where the concentrations of DDT and PCB are substantially higher. But even in those areas the toxicant concentrations in fish are well below the standard norms established in Estonia. By the data (Olsson et al., 2002), spatial distribution in concentration of DDT in Baltic herring muscle one of the lowest concentrations is found outside the Estonian coast.

CONCLUSION

At present time the contents of toxic chlororganic compounds (DDT; lindane, etc.) analysed in the fish (herring, perch, flounder, etc.) of Estonian coastal sea remain below standards established by FAO/WHO in food, in which case the content of toxicants in the food does not cause symptoms of illness in case of people (Roots, 1996; 2003; Roots and Simm, 2002). Even though the current levels of the investigated organochlorine compounds in fish do not represent a risk to humans, a continuing monitoring is needed to document the effectiveness of the international ban of the selected POPs.

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UNMIK

PROVISIONAL INSTITUTIONS OF SELF-GOVERNMENT INSTITUCIONET E PËRKOQSHME TË VETËQEVERISJES PRIVREMENE INSTITUCIJE SAMOUPRAVLJANJA

**The Ministry
of Environment and
Spatial Planning**

**Ministria
e Ambientit dhe
Planifikimit Hapësinor**

**Ministarstvo
Sredine i
Prostornog Planiranja**

Environmental Protection Division

STATEMENT ON OBSOLETE PESTICIDES IN KOSOVO/A

Kosova is situated in the center of Balkans' Peninsula and covers a surface of 10.887 km², and is believed to have approximately 2.5 million inhabitants, most of them are extensively engaged in agriculture.

Kosova as a small country that came out of war 4 years ago and is under the UN administration Mission in Kosova, besides the achievements and successes, it is also facing with different problems and essentially with the environmental problems. Apart from many another sources that have an efficient negative impact on the Environment, in Kosova pesticides present also a potential danger.

Before the war in Podujeva (town north-east of Kosova) existed a little factory for production of pesticides and which factory after the war was abandoned (the year 1999). An amount of pesticides and the equipment that was used for the process of production was left there. The pesticides were into steel barrels.

Because these barrels have been in very bad conditions, the local authorities and the representatives of the Ministry of Environment and Spatial Planning with the assistance of British KFOR troops who have purchased the 120 l plastic barrels, have restored the pesticide solutions from old metal barrels into plastic barrels.

Now, there are packed and enwrapped with plastic banding 64 plastic barrels with 7680 l of obsolete pesticides.

The processed (diluted) pesticides are of these types:

Semesan (phenil mercuric acetate),
Malathion,
2,4-D,
Rarox & Wararin (rodenticides),
Ambarin,
Zimotox,
Karathane.

Different institutions and organs proposed elimination of these pesticides, but no support was found from UNMIK

and KFOR, because these proposals were not in accordance with EU norms and standards for the elimination of obsolete pesticides.

For implementation of these works, a certain fund for elimination of these obsolete pesticides is required.

In Kosova, currently, there is no factory for production and processing of pesticides. The pesticides that are already there are being imported from European and neighboring countries. In some occasions, the pesticides are not controlled in details and happen that some of them are with nearly expired date, and after a short period the date expires. Then it comes to a problem for their elimination, because there is no special plant for this aim.

As for illustration, we give the fact that an amount of 80 t of pesticides was used in Kosova during 2002 (see Tab.).

THE AMOUNT OF PESTICIDES KG/L USED IN KOSOVA (in agriculture, 2002)

No	Pesticides	Amount (kg/l)	%
1	Fungicide	39784.23	49.84
2	Insecticide	23721.04	29.72
3	Herbicide	13134.10	16.45
4	Rodenticide	3152.14	3.95
5	Acaricide	16.50	0.02
6	Limatocide	16.50	0.02
	Total	79824.51	100

In Kosova there is no laboratory for analyzing pesticides, where the concentration of these pesticides could be determined with exactness, also there is no incinerator for elimination of obsolete pesticides.

Starting from this state and the fact that in Kosova there is a considerable amount of obsolete pesticides, which is expected to increase every year, we are expressing our concern and at the same time we are interested this issue to be included in the agenda of international programs for long-term solution of these problems.

ENVIRONMENTAL HEALTH RISKS TO FARMERS AS A RESULT OF PESTICIDES' MISMANAGEMENT IN KHANYOUNIS GOVERNORATE, GAZA STRIP

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ABSTRACT

Several poisoning and death cases were reported in Khanyounis Governorate as a result of mis-use and mis-handling of pesticides. Carcinogenic and internationally banned pesticides are still available in the markets in all the governorates of the Gaza Strip. This study aims to investigate the awareness and health issues of the farmers. Forty-five farmers were randomly selected to fill a questionnaire prepared for this purpose. The results showed that protective clothing are totally not worn during application of pesticides. Lack of storage faculties, unlicensed pesticide shops, improper disposal of the empty containers and smoking and eating during application are among the hot spots related to pesticides handling and application. Also, 44.5% of the farmers complain of health problems, of which headache, coughing, skin rashes and difficulty in breathing. Only 4.5% of the farmers attended general agricultural training courses. In conclusion the study suggests that the government, public, the non-governmental organizations and all the interested parties should cooperate in a collective and serious work to minimize these environmental and health risks.

INTRODUCTION

Khanyounis Governorate is located at the southern part of the Gaza Strip. The total area of Khanyounis Governorate is about 65 Km². The average rainfall is 250 mm/annum. The coastal 1-2 km wide belt along the Mediterranean Sea is covered with sand dunes of about 20-40 m above sea level. The population is about 200,000 people according to the survey conducted in 1997 (Al-Agha, 1995, 1997).

A significant progress was made in the environmental awareness studies on pesticide hazards and their health impacts in Third World countries during the 1990s. This is in fact true, when compared with the negligence of pesticide impacts during the last few decades. Surveys were conducted in different countries e.g. Brazil (Garvalho, 1990; Skalisz, 1991), India (PREPARE, 1991), Paraguay (Abbate, 1991), Pakistan (Chester et al., 1992), Kenya (Emanuel, 1992) and Sudan (Abd Rabou, 1996). These studies are considered important steps in strengthening the role of research in planning and policy-making. This leads to strengthening

the capacity building and awareness of the farmers, the governmental and the non-governmental organizations and/or institutions (Abd Rabou and Al-Agha, 1998).

In the Gaza Strip, agriculture is considered as the backbone of the income of many families. Farmers tend to use more fertilizers and pesticides than basically required to increase the agricultural production. Studies on pesticides and their hazards in the Gaza Strip are very limited. Safi and his colleagues started a modest and important work on pesticide hazards in the Gaza Strip. Safi et al. (1993) listed in their preliminary paper the mutagenic and carcinogenic pesticides used in the agriculture in the Gaza Strip. They indicated that about 75 pesticides are used in the area, 19 of which are internationally suspended and banned. Additionally, Safi (1995) displayed the pesticide - related problems in the Gaza Strip. These problems are: environmental pollution, pest resistance, non-target effects of pesticides and finally the health hazards related to pesticide use and mis-use.

PURPOSE OF THE STUDY

The objectives of study are to investigate the sources of the health risks that result during handling and application of pesticides. It is an attempt to understand the problem and to pinpoint the hot issues and/or items that could be placed in the priority list for any action. It is one of the high priority needs to attract the attention of the interested parties, planners, policy makers and decision makers to such hot issues in the environmental and public health.

METHODS OF STUDY

Forty-five small farms in Khanyounis Governorate, were randomly selected for this field survey. The survey was carried out by the authors using an especially prepared questionnaire. Arabic is the language of the questionnaire. It was tested by five experts in agricultural and environmental sciences. The farmers were then, individually visited and informed about the purpose of the study. They have been asked by the interviewer to participate, and were assured that all the information regarding their responses will be dealt as a top confidential matter. All these farmers were then interviewed and their responses were recorded in the questionnaire. The surveyor explained to the farmers any question which was not clear to them. The surveyor used to fill the questionnaire by himself. This study was carried out during June and July, 1997. The data were analyzed by descriptive statistical method.

RESULTS AND INTERPRETATION

The age of the interviewed farmers was found in the range between 20-65 years, with an average of about 37 years and standard deviation of 15. The average number of years of experience for these farmers is 14 years, ranging between 1-40 years, with standard deviation of 11. About 90% of the visited farms produce vegetables, while the rest mostly produces citrus. The area of these farms ranges between 1-40 dunums (1 dunum=1000 square meter), with an average of 6 dunums and standard deviation of 8. Other issues were surveyed during this work; the results are shown in Tables 1-12 and described below.

1. THE EDUCATIONAL LEVEL

The survey showed that 80.2% of the farmers finished the intermediate level of education, while 6.6% are totally non-educated, 13.2% are in the level of primary school, 15.8% are holding university degrees (Table 1). These results illustrate that the education level of the farmers is generally good, which means that over 85% of the interviewed farmers can read and write. This of course will help in any training courses to be held in the future. Such results are normally expected in the Palestinian society as a whole. This is because of the majority of the Palestinians in Gaza are educated as a result of the political, social and economic pressure during the last 4-5 decades. As most of the pesticides used in the Gaza Strip are imported from Israel, none of the farmers can read Hebrew language, by which most of the instructions are written. This suggests that any imported pesticides should have an Arabic translation of the instructions either by the manufacturers or the importers.

2. PESTICIDE SOURCES

The farmers were asked about the place from which they buy pesticides, all of them indicated that they get it from the local market (Table 2). This was not the case in Rafah Governorate, where some farmers get their pesticides from other sources, e.g. the extension services, the Israeli settlements in the area (Abd Rabou and Al-Agha, 1998). The pesticide local markets in the Gaza Strip are not governmentally supervised. Obtaining pesticides from the local shops is considered a source of risk to both farmers and crops. This is because the shop's owners are not qualified to guide the farmers to the instructions of pesticide use.

3. EATING, DRINKING AND SMOKING DURING HANDLING AND APPLICATION

Although eating and drinking are prohibited during handling and application of pesticides, only (2.2%) of the interviewed farmers admitted that they drink or eat, while others said that they do not do so (Table 3). Regarding smoking, 57.8% of the farmers are smokers, while 42.2% are non-smokers (Table 4). It was found that 15% of the smokers smoke sometimes during the handling and application of pesticides. The low percentage of the non-eaters or drinkers during work was explained to us by the farmers due to the fact that, they definitely know that pesticides are toxic and may rot to the human body during eating or drinking. The high percentage of smokers is attributed to the fact that all of them do not know that smoking could have harmful impacts on the human body during application of pesticides. Other smokers said that they do not smoke during work only because they cannot do it.

4. PROTECTIVE CLOTHING OR WORKING CLOTHES

Protective clothes must be worn during handling and application of pesticides. However, it was found that none of the farmers has real protective clothes. But what they have is just clothes for work, which are different from those clothes clothed by the farmer during his normal life. The definition of the protective clothes by these farmers is not more than "working clothes". We had seen many of these clothes used by the farmers and they are not more than second-hand or even third-

Education	Frequency	Percentage
Non-educated	3	6.6
Primary school	6	13.2
Preparatory school	10	22.2
Secondary school	19	42.2
University degree	7	15.8
Total	45	100

Table 1: Educational level of the farmers

Source	Frequency	Percentage
Local shops	45	100
Extension services	0	0
Others	0	0
Total	45	100

Table 2: Pesticide sources

Eating and drinking	Frequency	Percentage
Yes	1	2.2
No	44	97.8
Total	45	100

Table 3: Eating and drinking during pesticide handling and application

Smoking	Frequency	Percentage
Yes	26	57.8
No	19	42.2
Total	45	100

Table 4: Smoking during pesticide handling and application

Protective clothing	Frequency	Percentage
Yes	21	46.7
No	24	53.3
Total	45	100

Table 5: Wearing of Protective clothing (working clothes)

Storage	Frequency	Percentage
Special store	0	0
Home	36	80
Farm	9	20
Total	45	100

Table 6: Storage of pesticides

Disposal	Frequency	Percentage
Burial-burning	24	53.4
Throw way	20	44.4
Use	1	2.2
Storage	0	0
Total	45	100

Table 7: Disposal of pesticides' empty containers

Action	Frequency	Percentage
Clothes taken off directly	20	44.5
Finishing, Clothes taken off	22	48.9
No action, no bath	3	6.6
Total	45	100

Table 8: Drainage of pesticides on the body

Period (days)	Frequency	Percentage
1-3	17	37.5
4-8	21	46.7
<8	7	15.8
Total	45	100

Table 9: Pre-harvesting period

Training courses	Frequency	Percentage
Yes	2	4.5
No	43	95.5
Total	45	100

Table 10: Attendance of training courses

Disease	Frequency	Percentage
Yes	20	44.4
No	25	55.6
Total	45	100

Table 11: Diseases related to pesticides

Disease	Frequency	Percentage
Yes	4	8.8
No	41	91.2
Total	45	100

Table 12: Diseases not related to pesticides

hand clothes. Some of these clothes were found with several holes in it, and some were found as short-legged pants and short-sleeved shirts. Shoes were found occasionally worn, and socks were very rarely worn. Thus, the term -protective clothing- was applied here according to the definition of the farmers themselves. This does not mean that the authors agree on such status. It was found that 46.7% wear these clothes, while 53.3% use their normal clothes (Table 5). 90% of the farmers do not know that pesticides may rout to the human body through skin. Such a risky and striking result needs urgent and serious campaigns among the farmers to raise their awareness and the health risks which they are exposed to.

5. STORAGE OF PESTICIDES

One of the striking results of this study is that 80% of the farmers store pesticides in their homes or houses, while only 20% store them in the farms (Table 6). Some of the farmers were asked why they used their homes for pesticide storage and they answered that pesticides may be lost or stolen in the farm, because they do not have safe stores in their farms.

6. DISPOSAL OF EMPTY CONTAINERS

Most of the empty pesticide containers are considered as one of the dangerous hazardous wastes, if they were not thoroughly washed and rinsed after use. 53.4% of the farmers dispose of these containers either by burning or burial in the farm depending on the type of the material from which the container is made (paper, plastic or metal). 44.4% of the farmers throw these containers away in the farm or along its fence. Both of these do not rinse the containers after use. 2.2% of the interviewed farmers admitted that they could use these empty containers for domestic purposes when the size and the shape are affordable for some kinds of uses (Table 7). In the Third World countries, the use of the empty pesticide containers for domestic purposes is common.

7. DRAINAGE OF PESTICIDES ON THE HUMAN BODY/SKIN

The farmers were asked on their behavior when pesticides drain on their bodies during application. 44.5% said that they take their clothes off and wear others. While 48.9% stated that they do not care when pesticides drain over their clothes and/or bodies and continue their work, after then they will have a bath. The remaining 6.6% of the farmers said that they do not care and even do not bath after finishing their work; they just take their clothes off in the end of the day (Table 8).

8. PRE-HARVESTING INTERVAL

Pre-harvesting interval is the period which must be left between the application of a pesticide in the farm and the harvesting of a crop. This is to ensure that pesticide residue on the crop becomes within the acceptable and safe limits for human use (GIFAP, 1989). 46.7% of the farmers allow for only 4-8 days to harvest their crops, 37.5% were harvesting 1-3 days after application. 15.8% of the interviewed farmers waited from 9-15 days to harvest the crop (Table 9).

9. ATTENDING TRAINING AND/OR AWARENESS COURSES

4.5% of the farmers said that they attended training courses in various agricultural topics, where pesticides were part of the training material. While 95.5% of the farmers pointed out that they never attended such training courses and even they are not invited to these activities (Table 10). This is of course, backdated since they started their work, where we stressed on this point during our survey.

10. HEALTH COMPLAINTS

During the present survey, 44.5% of the farmers stated that they acquire some health complaints during application of pesticides (Table 11). On the other side 55.5% of the farmers indicated that they do not have any health problems during application of pesticides. 8.9% stated that they have diseases that are not related to their work, while the rest 91.1% pointed out that they do not complain of any disease (Table 12). Farmers who have health complaints during the application of pesticides, showed that they have coughing, headache, skin rashes, chest pains and difficulty in breathing.

DISCUSSION

The results of this survey showed that there are many dangerous and hot spots in the life and the health of the farmers during handling and application of pesticides. Several striking results were reported such as protective clothing, eating, drinking, and smoking during pesticide handling and application, pesticide waste disposal, storage and pre-harvesting period. Other issues were of high importance like the health complaints and the low percentage of farmers attending training courses. All these hot issues are of very dangerous impacts on the farmers' health and even the public health in general. The risk of pesticides to the human body depends on the exposure and toxicity. The long exposure periods are very dangerous on the human health, even if the toxicity is not high. On the other side toxicity of pesticides is variable from one type to the other. Long period of exposure of low

toxic pesticide could produce risk more than a high toxic pesticide with short period of exposure. In this study, some farmers did not give attention to the exposure period and even the routes of exposure. Such results indicate how the situation is, and these suggest an urgent and serious action. In order to minimize exposure awareness campaigns and training courses are strongly recommended to start soon. However, the issue of the protective clothing is a very hot spot to which the attention of the government and the farmers must be directed. It is very sad situation that none of the farmers wears real and healthy protective clothes.

CONCLUSION

Khanyounis Governorate depends mostly in the agriculture as the main source of income to many of its population. Several poisoning and death cases were reported in this Governorate in the last few decades as a result of pesticide mismanagement. Several types of carcinogenic and internationally banned pesticides are still in use in the Gaza Strip as a whole. The survey indicated that the situation in Khanyounis Governorate is horrible regarding the awareness of the farmers on how to deal with pesticides in a safe and healthy way. It is very obvious that the most dangerous issue is the protective clothing, where none of the farmers found wearing a safe and healthy clothes. Another important issue which is the storage and disposal of pesticides, where about 80% of the farmers uses their homes to store these toxic materials. Eating, drinking and smoking while application and handling of pesticides was found also a hot spot. Pre-harvesting period is not strictly followed by the farmers. The health complaints (coughing, headache, skin rashes, chest pains and difficulty in breathing) were expected as most of the activities related to pesticide handling and application, were done in an improper and unhealthy way. These are the important components of the environmental health and awareness among the farmers in Khanyounis Governorate.

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INCREASE OF BREAST CANCER INCIDENCE IN ARMENIA: PROBABLE ROLE OF PESTICIDES APPLICATION

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INTRODUCTION AND OBJECTIVES

A number of pollutants (pesticides, industrial chemicals, etc.) are potentially dangerous for the living organism, since they are known to activate the formation of toxic intermediates in the organism. A relationship between oxygen activation by pollutants and their toxicity has been suggested due to highly reactive oxygen species formation. As a result, we can use the level of oxygen radicals in the organism as criteria for the harmfulness of the environmental pollutants [1].

Molecular criteria were developed for evaluation of toxicity of different substances used as agro- and industrial chemical substances, which have a potential toxic effect. In particular, in our reports and publications on numerous pesticides, we described that some of them possessed mutagenic and carcinogenic activity [2]. It was shown that the key agents of their toxic action are superoxide radicals [1]. Concomitant with the metabolism of environmental agents such as pesticides, nitrates and industrial chemicals, the rate of superoxide radicals' generation is greatly elevated. Therefore, we consider the high level of superoxide radicals as one of the risk factors.

Apparently, a number of pesticides are not considered direct carcinogens, but in the human organism, carcinogenic metabolites are formed due to the metabolism. There exists the combined effect of two and/or more pesticides as well. The carcinogenic effect itself is a result of joint combined action of pesticides or their metabolites. That is why, to our opinion, the determination of concrete pesticides in human blood samples is not purposeful [3].

Armenia was one of the regions with intensive pesticide application. In the 1980s the territorial load of pesticides in agriculture exceeded the average for the Soviet Union more than 20 times. In 1984 high concentrations of organochlorine pesticides -i.e. DDT, officially forbidden in 1970, and the metabolite of DDT, DDE - were registered in 20% of samples taken from arable lands in the regions of Ararat, Oktemberian, Etchiniadzin, Artashat, Tumanian, Gugarak and Noemberian. DDT concentrations in samples from cultivated land in the Ararat region amounted to 0.02 -0.04 mg/kg in potato fields, 0.06-0.4 mg/kg in samples from orchards, while DDE residues were found at the level of 0.45 mg/kg. DDT and DDE residues in grape orchards were found at 0.3-0.85 and 0.08-0.8 mg/kg, respectively. Excessive contamina-

tion with pesticides such as DDT, DDE, dieldrin, aldrin and endrin was found in 2.56% of the tested products, mainly in meat, with potentially adverse effects on human health through accumulation in the food chain. [4]. Till now "fresh" contamination is observed in some regions of Armenia: residues of banned and/or obsolete pesticides are found in samples of water, soil and foodstuffs.

In 1995-2002, according to data of the Department of Statistics and the Centre of Oncology (Ministry of Health, Republic of Armenia), the incidence of breast cancer was on the 3rd place after the cancer of lungs and gastrointestinal tract. Breast cancer, as a known life-threatening malignant lesion in women of many developed countries, has a stable 1st place amongst other oncology states in women. In Armenia there is also a stable tendency to the increase [5].

Data indicate that the stable increase was observed as to the mortality index (as % of morbidity) of breast cancer. In 1997, mortality due to breast cancer was 57.3% (28% proceeded within the 1st year). A similar tendency is observed till now. Such unfavourable indices as well as the tendency towards their worsening are, apparently, conditioned by a number of causes of both socio-economic and environmental character.

Our researches were aimed at the study of medical (carcinogenic) after-effects, probably resulting from pollution of the environment due to pesticide application. It was of both importance and interest to reveal prevalence and morbidity of breast cancer, by the use of specific tumour markers. It would be of high significance to reveal molecular mechanisms of tumour incidence/development through the probable role of pesticide impact in incidence of breast cancer, based on the analysis for tumour markers and generation of superoxide radicals.

MATERIAL AND METHODS

193 women with different oncology problems of mammary glands were directed from the hospitals of Armenia and examined at the Clinical Diagnostic Department (NIH, Armenia). 89 women had the diagnosis of breast cancer; in 35 cases breast cancer was diagnosed later on. 69 women had high risk of breast cancer incidence based on mammography checks.

Patients involved two age groups:

- Group 1 – patients aged 40-49,
- Group 2 – patients aged 50-69.

In recent years, suitable and reliable methods of immune-enzyme tumour markers testing in blood serum are widely used. Tumour markers present themselves a group of factors detected in malignant and malignant growth associated cells. The diagnostic significance of tumour markers is very high in combined testing; the procedure itself is suitable enough. It is especially urgent for the screening and early diagnostics. Tumour markers are irreplaceable in the screening/monitoring of both the disease and the treatment process. The point of prime importance is that the recurrence and metastasis can be revealed with the help of tumour markers six month prior to the clinical manifestation of the disease or even earlier.

Enzyme Immunoassays (EIA) for the quantitative determination of cancer antigens CA 15-3, CA-125, CA 19-9, CEA, HgH, beta-2M in human serum (DRG International, Inc., USA; Syntron, USA) were used.

The Equipment used for early cancer diagnostics included: Microwell Strip Reader – Stat Fax® 303, Microwell Washer – Stat Fax® 2600, Incubator/Shaker – Stat Fax® 2200 Chemistry Analyzer – Stat Fax® 1904 (AWARENESS Technology, Inc., USA).

Superoxide Dismutase (SOD), a known scavenger of superoxide radicals, was evaluated by the ability of aliquots of blood serum to inhibit the colour reaction of reduction of nitro blue tetrazolium with the formation of phormazan by Nishikimi et al., 1972 [6].

The diagnostic significance of tumour markers is very high in such combined simultaneous testing of SOD activity.

RESULTS AND DISCUSSION

It was revealed that 97% of women from all groups CA 15-3 had tumour marker level above the norm. The analyses of the special questionnaire demonstrated that amongst those examined, there were women from rural districts of intense uncontrolled application of organochlorine, organophosphorus pesticides, nitrates and other agrochemicals.

In both age groups with CA 15-3 above the normal level, our findings revealed a decrease of such an important protective system as SOD activity as compared with the control group of healthy women. It must be emphasised that in Group 1 the decrease made 33% and in Group 2 it was 58%.

The results of our previous experimental studies in laboratory animals showed that formation of superoxide radicals underlies the molecular mechanisms of toxic, carcinogenic, mutagenic and delayed toxic effects of organochlorine pesticides, some phosphorous agrochemicals, and nitrates (2).

Thus, the low level of SOD activity revealed in blood serum of patients might be the result of either generation of superoxide radicals due to the effect of chemicals (pesticides) or due to a direct effect of pesticides on the protec-

tive system of the living organism. Superoxide radicals have a probable role in the mechanisms of breast cancer development, especially in women aged 50 and older.

In both Group 1 and Group 2 our analyses revealed no such correlation in concern of ovarian cancer tested by means of tumour marker CA 125.

It cannot be excluded that the SOD activity revealed could be the result of environmental hazards and other known factors.

Data and findings obtained dictate the necessity to suggest the following programme for comprehensive studies:

1. To perform screening examinations in a cohort of women of reproductive age in order to reveal tumour incidence in rural districts (see the Table below);
2. To trace the relationship between the
 - geographic location
 - pesticide application
 - occupational exposure
 - consumption of food polluted by pesticides, etc.
3. To establish the relation between
 - the quantity of pollutants (pesticides) used,
 - amounts, acquired by the individuals from risk groups via the food chain, directly or indirectly, and
 - cancer prevalence.
4. To draw correlation of tumour marker levels with the SOD values and intense application of pesticides;
5. To confirm probable significance of environmental factors (pesticide load) in incidence, onset and development of breast cancer.

Tumour localisation	Laboratory tests recommended
Breast	CA 15-3, CEA, Ferritin, MCA
Uterus (body, neck)	CA 125, AFP, HgH, b-2M, CEA
Ovaries	CEA, CA 125, b-2M, AFP, HgH

Table: Tests recommended for screening medical examination in order to reveal groups at risk in female population of areas with intense agriculture (application of pesticides)

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RISK ASSESSMENT OF ATRAZINE POLLUTED FARMLAND AND DRINKING WATER: A CASE STUDY

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ABSTRACT

In late May 1997, a large-scale pollution of Atrazine took place in the rice-growing area of Changtu county, Liaoning province, China. Over 2,800 hm² of rice fields were polluted due to irrigation from Atrazine polluted Tiaozi River and Zhaosutai River, leading to a direct loss of 42 million RMB (about 4.4 million EUR).

Four years after the accident, Atrazine residues in the local agro-ecosystem were measured at Bamiancheng and Baoli, two-rice growing areas downstream Tiaozi River and Zhaosutai River, respectively. The survey indicated that higher Atrazine concentration detected in lightly polluted soil at Baoli as compared to that in heavily polluted Bamiancheng was likely due to higher organic matter and higher clay content, which contributed to keep more Atrazine from leaching out of soil profiles. Although Atrazine can still be detected in rice grains, surface water as well as groundwater, the concentrations were below the criteria for human consumption.

It was concluded that Atrazine is persistent, highly mobile and bioaccumulative. Therefore it may pose potential threat to human health through food chain or drinking water in the long term.

INTRODUCTION

Atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-1,3,5-triazine) is a commonly used herbicide for corn, sugarcane, grain sorghum, tea and fruits. Since its introduction to China in the early 1980s, Atrazine consumption in China has been increasing by 20% each year (Shu, 2000).

With increasing production and consumption of pesticides, pesticides-related pollution cases tend to increase in China. From July 1995 to August 1996, more than 2000 cases of pesticides pollution have been reported in 19 provinces of China. About 130,000 hm² of farmland were polluted to various degrees and the consequent losses were 500 million RMB (about 52.5 million EUR). Overall losses for the whole of China during that period were estimated to be 1 billion RMB (about 105 million EUR) (Jiang and Hua, 2000).

Despite its effectiveness against annual gramineous herbs, Atrazine poses a threat to ecological safety because of bioaccumulation and persistence. Study by Soloman showed that half life of Atrazine was 244 days at pH 4 and 25 °C (Soloman, 1996).

Atrazine has been detected in surface waters such as rivers, lakes, gulfs as well as groundwater in many EU countries (Siebers, 1994). The maximum contaminant level of Atrazine in drinking water is 0.1 µg l⁻¹ in EU countries and 3 µg l⁻¹ in the US and China. At low soil pH, protonized Atrazine becomes more hydrophilic and is likely to move downwards with soil water and reach groundwater. Atrazine leaching is also affected by soil properties such as soil organic matter and clay content, which will determine the partition coefficient of Atrazine between soil particles and water. The higher organic matter and clay content, the stronger Atrazine bonded to soil solid phase. An investigation conducted in Nebraska, USA revealed that 0.07% of total Atrazine applied to a sandy loam infiltrated down to 1.5m below surface (Capriel *et al.*, 1986). In the case of paddy fields, frequent irrigation facilitates Atrazine leaching. It is proposed that leaching and degradation are the two main pathways of Atrazine dissipation in paddy fields while the contribution of surface runoff is limited (Alissara *et al.*, 2001).

In late May 1997, a large-scale pollution of Atrazine took place in the rice-growing area of Changtu County, Liaoning province. More than 2,800 hm² of rice fields were polluted as a consequence of irrigation from Atrazine polluted Tiaozi River and Zhaosutai River. The upper reaches of the two rivers were polluted to different degrees by Atrazine due to accidental leakage from a state-owned pesticides manufacturer in the nearby Siping city, Jilin province. Rice seedlings died out in many polluted fields, leading to a direct loss of 42 million RMB (about 4.4 million EUR).

A six-month monitoring was conducted right after the accident. According to the monitoring report issued by Pesticides Safety Evaluation Centre (PSEC), Department of Chemistry in July 1997, Atrazine concentrations detected around Bamiancheng ranged from 0.06 to 0.29 mg l⁻¹ in Tiaozi River, from 0.23 to 0.36 mg kg⁻¹ in soils and from 1.07 to 2.26 mg kg⁻¹ in young rice shoots. In contrast, Atrazine concentrations detected around Baoli were from 0.03 to 0.06 mg l⁻¹ in Zhaosutai River, up to 0.08 mg kg⁻¹ in soils and up to 0.28 mg kg⁻¹ in young rice shoots. Obviously, Atrazine pollution was more serious around Bamiancheng than around Baoli (PSEC-R9734001ST, 1997).

Based on data obtained from field studies and pot trials, remedy measures, including well irrigation, change of crops, postponing transplanting, deep plowing, organic amendments and addition of Atrazine-degrading bacteria, were taken to resume agricultural production in the polluted area.

Atrazine behaviors in the environment have been intensively studied in the past several decades. The aims of these studies were to (1) determine Atrazine residuals in soils, rice grains and drinking water in the polluted area four years after the accident, (2) to gain a better understanding of the persistence and mobility of Atrazine in the multimedia environment and (3) to assess Atrazine exposure risks in the polluted area.

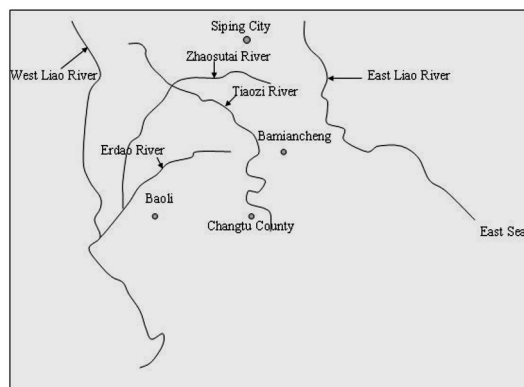


Figure 1: A schematic map of the water system in Changtu County

MATERIALS AND METHODS

1. Site description

Changtu County is located in the north of the northeast province of Liaoning China (E 123° 32' - E 124°26', N 42°33' - N 43°29') and adjacent to Siping city of Jiling province. Zhaosutai River and Tiaozi River are the two main irrigation water sources for the rice growing area of Baoli and Bamiancheng, respectively (see Figure 1).

2. Sampling

In October 2001, vertical distribution of Atrazine was sampled at three locations of Baoli and Bamiancheng, respectively. Soil samples were taken at a depth of 0-20cm, 20-40cm, 40-60cm, 60-80cm and 80-100cm, respectively. Meanwhile, rice grain samples were also taken at the same locations. Surface water samples were taken from a nearby reservoir or tap water. Underground water samples were taken from wells at 10 meters depth.

3. Sample analysis

Soil pH was analysed with compound electrodes (Soil: H₂O=1:2.5). Soil organic matter was measured using potassium dichromate oxidation method. Soil particle distribution was determined using a densimeter. As shown in Table 1, the alkaline paddy soil at lightly polluted Baoli has higher organic matter and clay content as compared to that at Bamiancheng.

Atrazine in soil and plant samples was extracted by ultrasonic and analyzed with GC-NPD after purification (Li *et al.*, 2003). Atrazine in water was extracted using solid phase extraction techniques and analyzed with GC-MS as described by Ren *et al.* (Ren *et al.*, 2002).

RESULTS AND DISCUSSION

1. Vertical distribution of Atrazine in soil profiles

Vertical distribution of Atrazine was shown in Figure 2. Statistically, there was no significant difference among Atrazine concentrations at different layers either at Baoli or

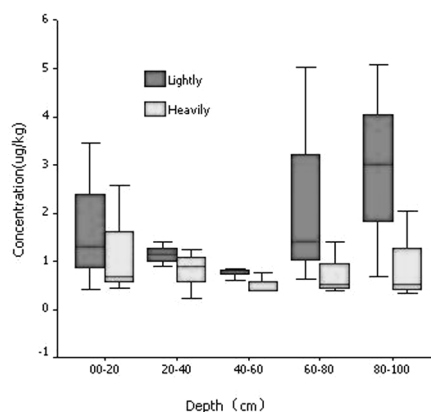


Figure 2: Vertical distribution of Atrazine in soils

at Bamiancheng. However, Atrazine residuals in soil profiles were significantly higher in lightly polluted soil at Baoli than in heavily polluted soil at Bamiancheng ($p < 0.05$). As the partition coefficient of Atrazine is determined by soil organic matter and clay content, it is therefore understandable that dissipation of Atrazine via leaching will be favoured in soils with low organic matter or coarse texture. A possible explanation for higher Atrazine residuals in lightly polluted soil at Baoli was due to its higher organic matter as well as much higher clay content as compared to heavily polluted soil at Bamiancheng (see Table 1).

2. Atrazine concentrations in rice grain

Four years after the accident, Atrazine can still be detected in rice grains both at Bamiancheng and Baoli. Atrazine residual in rice grains ranged from 0.62 to 1.25 $\mu\text{g kg}^{-1}$ at Bamiancheng and from 0.54 to 4.25 $\mu\text{g kg}^{-1}$ at Baoli. In both cases, Atrazine concentrations were lower than the French maximum residue limits of 5 $\mu\text{g kg}^{-1}$ for corn.

3. Atrazine concentration in drinking water

Analysis of Atrazine concentration in local surface water and groundwater showed that Atrazine concentrations were between the maximum contaminant level of 0.1 $\mu\text{g l}^{-1}$ established by EU and of 3 $\mu\text{g l}^{-1}$ established by US for drinking water. For instance, at heavily polluted Bamiancheng, Atrazine concentrations were higher in surface water (ranging from 0.10 to 0.32 $\mu\text{g l}^{-1}$) than in groundwater (ranging from 0.07 to 0.10 $\mu\text{g l}^{-1}$). Atrazine concentration in the groundwater of lightly polluted Baoli was below 0.0026 $\mu\text{g l}^{-1}$.

CONCLUSIONS

Four years after the cut-off of the pollution source, Atrazine can still be detected in the agro-ecosystem of the affected area. Although Atrazine concentration in rice grains and drinking water was below or close to the criterion, due

Location	Pollution status	OM %	pH	Sand %	Coarse silt %	Fine silt %	Clay %
Baoli	Lightly polluted	1.37	8.08	25.03	30.50	14.49	29.96
Bamiancheng	Heavily polluted	1.20	6.86	16.44	53.07	22.06	8.41

Table 1: Selected properties of soil tested

to its long half time and bioaccumulation, Atrazine could still be an environmental concern and needs to be addressed.

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PESTICIDES POLLUTION AS ONE OF THE ANTHROPOGENIC LOAD FACTORS IN CHERNOBYL ZONE

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The Exclusion Zone of the Chornobyl Nuclear Power Plant (NPP) is the most polluted by basic radionuclides territory that measures 2,044 km². Its population was evacuated in 1986 and any kind of housekeeping was forbidden. At the same time, the results of recent research work show that the Exclusion Zone is a very effective barrier to the expansion of radionuclides in the inhabited territories of Ukraine and Belarus. Influence of pesticides as one of the anthropogenic factors upon the water quality in the Pryp'yat river within the territory of the Exclusion Zone for the period of 1989-2003 has been researched. Also questions regarding the influence of the Exclusion Zone on the waterbodies of the Pryp'yat river basin has been explored.

The territory of Exclusion Zone belongs to the physical and geographic zone of mixed forest so called Pryp'yat Polissya. Its territory pertains to the waterbasin of the Pryp'yat river, the tributary of the main water-way of Ukraine – the Dnipro river.

The Pryp'yat river crosses the Exclusion Zone from the North West to South East and flows into the Kyiv reservoir. Total length of the river is 780 km, watershed square is 116000 km². Within the territory of the Exclusion Zone the river length from Dovlyady village to the mouth is near 50 km, and watershed square is 2000 km².

The basin of the Pryp'yat river represents a system of interconnected waterbodies influenced by a number of factors of anthropogenic origin. It is expressed by index-

es which negatively characterize hydrological and chemical condition of the river. For instance, water consumption of Dnipro-Bug canal that results in shallowing and degradation of a riverbed aggravate the hydrological regime of upper part of the river. Downstream 80 barriers for fish-catching for fishery supplement the list of anthropogenic factors. These constructions enhance the processes of sedimentation. According to the extreme overloading on the river ecosystem and exceeding the processes of pollution over self-renewal one the upper part of the river (from Richytza village of Volyn region to the border on Rivne region) must be cleared away. On the whole, the main anthropogenic factor of the Pryp'yat river pollution (outside the Chornobyl zone) is certainly agriculture, especially melioration, and excessive usage of moistened lands. Almost 15% of its waterbasin is meliorated, unfortunately it is mostly land directly adjoining to the Pryp'yat and its tributaries riverbeds. Practically during development of melioration plans neither a number of over-moistened lands within different riverbasins nor a specific gravity of reclamation loading was taken into consideration. As a result drained systems embrace 12-15% of soils of semihydromorphous and automorphous row so that they must not be hydromeliorated, and overdrainage of these soils results in their degradation, carrying-out of useful substances and finally contamination of waterbodies.

The developed agricultural complex of urbanized territories is characterized by release of surface water into waterbodies, which contributes 80% of contamination. The volume of substances carried-out from agricultural territories by surface waste water depends on the structure of watershed (the percentage of woodland, waterlogging, ploughing), its meliorative transformations, kind and concentration of applied fertilizers, number of livestock, population density, precipitations, relief (down gradient), soil characteristics etc.

In such a way entering the Exclusion Zone water of the Pryp'yat river contains a range of compounds of anthro-

Place	N,n-DDT	N,n-DDE	DDD	Σ-DDT	α-hezachl orcyclo hexane	β-hezachl orcyclo hexane	γ-heza- chlor- cyclohe- xane	Σ-heza chlor cyclo- hexane	aldrin	Hepta chlor		ΣDDT+Σ heza- chlor- cyclo- hexane
The Pryp'yat river (left bank)	2,4*10 ⁻⁵	2,4* 10 ⁻⁶	2*10 ⁻⁷	2,7*10 ⁻⁵	8,0*10 ⁻⁷	N/A	5,0*10 ⁻⁷	1,3* 10 ⁻⁶	6*10 ⁻⁸	N/A	N/A	2,8*10 ⁻⁵
The Nesvich river	6,3*10 ⁻⁵	1,2*10 ⁻⁶	1*10 ⁻⁶	6,5*10 ⁻⁵	1,6*10 ⁻⁶	2,0*10 ⁻⁶	5,0*10 ⁻⁷	4,0*10 ⁻⁶	N/A	N/A	4,0*10 ⁻⁸	6,9*10 ⁻⁵
Magistral canal- 1, Paryshiv village	6,0*10 ⁻⁶	3,6*10 ⁻⁶	N/A	9,6*10 ⁻⁶	8,0*10 ⁻⁷	N/A	5,0*10 ⁻⁷	1,3*10 ⁻⁶	1,5*10 ⁻⁷	N/A	3,2*10 ⁻⁷	1,0*10 ⁻⁵
MAC, mg/ dm3				0,002				0,02	0,002		0,0003	

Table 1. Chlororganic pesticides concentration in the Chornobyl Exclusion Zone waterbasin, mg/dm³

pogenic origin including nearly 70% of Caesium-137 of total amount getting the Kyiv reservoir. Moreover, nearly 65% of Strontium-90 comes in waterbody on the territory within Dovlyady village and Chornobyl that makes worse radioactive characteristics of water. To compound the problem widespread flowing slashes on the watershed and overloaded riverbed.

The biggest tributary of the Pryp'yat river within the Chornobyl Exclusion Zone is Uzh river which runs in the South part of Zone and flows into Pryp'yat river downstream Chornobyl town. The Zone contains 20% of waterbasin of the Uzh river. There are two left-bank tributaries such as Hrezlya and Illya and three right-bank tributaries of the Uzh river such as Veresnya, Radynka and Bober, which run on the territory of the Zone.

Entirely the waterbasins of right-bank tributaries of the Pryp'yat river Sahan and Hlynyski rivers locate within the Zone. In the Southern part of the Zone Pogonyanskyy canal flows into the Pryp'yat river from the left bank. Its waterbasin lies on the territory of Belarus and its hydrological regime is negatively influenced by built supporting dams and locks. It became a reason of drastic decrease of drainage to the Pryp'yat and Braginka rivers which directly flow into the Kyiv reservoir. Nowadays the Pogonyanskyy canal is stopped up in Borschivka village and its drainage directly to the Pryp'yat river occurs only in near-mouth part of the watershed.

Hydrological network of the Chornobyl zone also includes closed and weakly flowing waterbodies, among them the Starik and Azbuchin lakes, Semihodsk and Pryp'yat bays, and a number of waterbodies of left-bank Pryp'yat flood-plain. Near the Chornobyl NPP along the right bank of the Pryp'yat river there is a reservoir-cooler of the plant. Its waterlevel is six metres higher than the river's one, so that it causes constant infiltration process through the bottom and dam of the reservoir-cooler of the Chornobyl NPP. Annual drainage of the Pryp'yat river

averaged 12,7 cubic km, 0,05-0,08% of this number belongs to the infiltration process from a mentioned reservoir-cooler.

Nowadays within the territory of the Exclusion Zone there are no functioning agricultural fields that means this territory is not exposed to agricultural loading and considered as control territory to compare agricultural loading on the ecosystems of other fields.

The assessment of pesticides concentration in the surface waters of the Exclusion Zone is given in table 1.

To define the concentration of stable chlororganic pesticides in the surface waters at the beginning of autumn three samples were taken from the main waterbodies on the left bank of the Pryp'yat river within the Exclusion Zone. Analysis conducted on gas chromatographer "Tsvet-500 M» testifies the presence of six-seven kinds of pesticides (S DDT+ X hexachlorocyclohexane): the Pryp'yat river – 0,000028 mcg/dm³, the Nesvich river – 0,00069 mcg/dm³, Magistral canal-1 – 0,00001 mcg/dm³ (table 1).

In such a way the main reasons for worsening of chemical composition of little rivers water and canals of meliorative systems that correspondingly reflects the water quality in the Pryp'yat river are increasing the carrying capacity of riverbeds and flood-plains of the Pryp'yat river, neglect of meliorative systems within the Exclusion Zone (where lock screens stay closed), damming of flood-plain territories and pumping out water highly contaminated by organic substances, and flooding.

Consequently, the concentration of pesticides in the waterbodies of this Zone some times lower than in surface waterbodies running the humidic zone of Ukraine outside the Chornobyl zone. This fact underlines more intensive decrease of retrospective contamination in the Zone comparing with other regions where chlororganic pesticides are being used in the agricultural sector.

THE ACWA PROGRAM: AN ALTERNATIVE APPROACH, PROGRAM MANAGER ASSEMBLED CHEMICAL WEAPONS ALTERNATIVES

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INTRODUCTION

The Army's technologies for destroying stockpiles of chemical weapons have been debated for many years by environmentalists, community members living near the stockpile sites, scientists, government and regulatory agencies, and other interested parties. The Department of the Army historically has supported incineration as its preferred method for the disposal of chemical weapons.

The Program Manager Assembled Chemical Weapons Assessment (PMACWA), which was charged with assessing alternatives to incineration for assembled chemical weapons, developed a process for evaluating, selecting and demonstrating technologies with significant, diverse public participation. PMACWA brought together key stakeholders from private and industrial sectors, various Army agencies, and regulatory communities in an open and collaborative process. As a result, all participants reached a consensus and supported the decisions and conclusions of the program as both technically sound and publicly acceptable.

THE ORIGINS OF ACWA

In 1985, the U.S. Congress directed the disposal of all stockpiled U.S. chemical weapons and agent. As a result, the U.S. Army Program Manager Chemical Demilitarization (PMCD) was established and charged with the responsibility for the destruction of the nation's chemical weapons stockpiles, located at nine sites across the country. To accomplish its mission, PMCD began preparations to implement the proven incineration technology at each of these sites. Over several years, this effort was met with opposition from various environmental advocacy groups at many of the stockpile sites.

"Opponents began using the environmental permitting process to mount legal challenges to the use of the incineration, which started to impact the Army's schedule, budget, and it increased the public risk associated with the continued storage of chemical weapons," recalled Program Manager Michael A. Parker. "Congress recognized this and reacted with a plan, which I think benefited both the public and the Army."

In 1996, Congress passed Public Law 104-208, which charged the Under Secretary of Defense for Acquisition and Technology with designating a program manager to identify, demonstrate, and evaluate not less than two alternative

technologies to baseline incineration and report the conclusions of the assessment to Congress. Congress also suspended the funding to construct baseline incineration facilities at the Blue Grass Army Depot in Kentucky and the Pueblo Chemical Depot in Colorado pending receipt of the findings and subsequent Congressional actions. The first result of this law was the selection of Michael Parker as program manager and the establishment of the Assembled Chemical Weapons Assessment (ACWA) program.

THE ACWA APPROACH

PMACWA realized early on that a public participation program would be as critical as its technical program in ensuring the success of its mission. To facilitate the process of working with various stakeholders the program enlisted the support of a non-profit public policy organization specializing in mediation to convene the various stakeholders into what became the Dialogue on Assembled Chemical Weapons Assessment (hereafter referred to as "the Dialogue"). The non-profit organization identified key stakeholders from the Department of Defense (DOD); state, and federal regulators; national activist groups; and a diversity of citizen interests from all nine stockpile sites. The group of some 35 stakeholders that comprised the Dialogue worked side-by-side with the PMACWA staff from the outset of the program, through the original procurement process, continuing with the testing, evaluation, and reporting of the technologies being demonstrated, and culminating in the decision-making process for technology selection at Pueblo and Blue Grass. The group's overall goal was established as the following:

"Draw on a wide range of experience, perspectives and expertise in support of efforts to identify, demonstrate and deploy safe, effective and broadly acceptable methods for disposing of chemical munitions and any resulting materials and/or waste streams."

To accomplish its goal, the Dialogue planned to fulfill the following objective:

"Solicit stakeholder input into the Congressionally-mandated program at key decision-making points during the process, including but not limited to: assisting with the development of criteria for comparing technologies, providing input into the assessment of alternative technologies, and aiding in the determination of appropriate locations for technology demonstrations."

Dialogue meetings were open to the public, and the group gave all attendees the opportunity to provide comments for consideration. Meetings were held at or near stockpile sites to encourage local residents to attend, or in Washington, D.C., to facilitate DOD and congressional participation.

In addition to meetings, ACWA supported various outreach initiatives since the program's inception. These initiatives focus on two primary objectives: 1) to provide information, and 2) to provide opportunities for public involvement. The goal was to provide the public with as much information as possible about the technologies, given the constraints of a procurement-sensitive evaluation process, and to encourage them to provide input into the decision making process.

One key mechanism that helped PMACWA conduct a successful program was a combination of four Dialogue members and a support contractor comprising a Citizens' Advisory Technical Team (CATT). The CATT became integral to the process and provided an independent review of the program for the Dialogue. CATT members signed confidentiality agreements allowing them to serve as the Dialogue's "watchdog" at many PMACWA internal meetings, including those dealing with procurement-sensitive information. By participating in meetings normally open only to PMACWA staff, the CATT provided Dialogue members with assurances that the technical program was being executed according to the commitments PMACWA had made to the Dialogue. The CATT also provided a mechanism for stakeholder input into the program's technology selection and evaluation process. The CATT thus ensured maximum communication between PMACWA and stakeholders while respecting the government's legal and ethical responsibility to protect proprietary and trade secret information contained in proposals and other documents submitted by technology providers.

THE ACWA PROCESS

PMACWA set out to accomplish several milestones in order to achieve this larger mission. With the Dialogue and public participation program in place, the program began to focus on three programmatic phases:

1. Development of criteria by which to solicit and select technologies for evaluation. This challenging process was completed in less than three months with program staff drafting the initial document based on their expertise and public documents gathered from various Chemical Demilitarization Citizens' Advisory Commissions (CACs) and other groups noting the attributes they desired in alternative technologies. The draft was then worked with the public and technology providers until the criteria were finalized. The complex process comprised three tiers of criteria, including:

Threshold Criteria: For use in screening proposed technologies, this set of criteria outlined the minimum requirements technologies had to meet to be considered by the program.

Demonstration Selection Criteria: For the detailed evaluation of specific technologies, this set of criteria was used by PMACWA to select technologies for demonstration and included technical and business factors. The technical factors were sub-divided into process efficacy, safety and human health and environment.

Implementation Evaluation Criteria: For the assessment of the demonstrated technologies, this criterion was similar to Demonstration Selection Criteria and was used as the basis for all recommendations to Congress.

2. Assessment of technologies for demonstration. The goal of this phase was for PMACWA to evaluate proposed technologies using available data, and to incorporate additional data requested from the technology providers. In October 1997, task order contracts were awarded to seven companies with promising technologies. Based on a technology evaluation process that assessed the submitted proposals, the initial awards funded work by the technology providers to fill in identified data gaps, so that more robust evaluations could be conducted. An evaluation of the completed data sets led to the award of a second

task order to six of the technology providers that required the offerors to submit demonstration work plans.

3. Demonstration of technologies. Due to funding limitations, only three technology providers were awarded demonstration contracts in July 1998, which initiated "Demonstration I." On October 25, 1999, Public Law 106-79 provided additional funding and allowed PMACWA to conduct demonstrations for the remaining three technology providers, which initiated "Demonstration II." Demonstrations were designed to be a series of validation tests for the critical unit operations of each technology as determined by PMACWA. Test plans focused on the means by which to validate performance of the technology processes, to characterize the process intermediates and final effluents, and to establish confidence that they could be incorporated into an overall system or "total system solution." Government personnel conducted all tests using existing government facilities. The program staff worked in an iterative process with test installation representatives, support contractors, members of the CATT, and the technology providers in performing detailed planning activities. The performance of the process demonstrations and the analytical results were reviewed and evaluated using the Implementation Criteria. Collectively, two supplemental reports were submitted to Congress and indicated that four technologies to demilitarize assembled chemical weapons were validated during Demonstration I and Demonstration II. In each of these reports, the Dialogue drafted and agreed to a several page consensus letter that noted recommendations for Congress regarding the ACWA program.

Once it became clear that alternative technologies could be demonstrated successfully, Public Law 105-261 was passed, which directed that PMACWA carry out "activities necessary to ensure that an alternative technology for the destruction of lethal chemical munitions can be implemented." As a result, PMACWA expanded its focus. In order to establish program requirements, to prepare procurement documentation, to develop environmental documentation, and to prepare to award a contract for the design, construction, and operation of a pilot facility for the technology, a series of Engineering Design Studies were initiated for the four validated technologies. These studies were designed to obtain further data required to support the certification decision of the Under Secretary of Defense for Acquisition, Technology, and Logistics, as well as to support solicitations for a full-scale pilot facility.

PMACWA worked with environmental regulators throughout the technology assessment and selection process to ensure environmental compliance and public safety under the purview of the National Environmental Policy Act. An Environmental Assessment was developed during the demonstration phase, the result of which produced a finding of no significant impact. Site-specific environmental strategies were implemented in compliance with federal and state laws governing transportation of materials, handling and disposal of waste, and potential air and water emissions. Environmental Impact Statements were developed at several stages of the process. In May 2002, the program's final programmatic EIS, Environmental Impact Statement for the Design, Construction, and Operation of One or More Pilot Test Facilities for Assembled Chemical Weapon Destruction Technologies at One or More Sites, was published.

In addition to preparing its own programmatic EIS, PMACWA provided support to PMCD as that program prepared site-specific EISs for Pueblo and Blue Grass.

In July 2000, the Under Secretary of Defense for Acquisition, Technology and Logistics, in his role as the DoD Acquisition Executive (DAE), requested a review of all aspects of the Chemical Demilitarization Program, including the ACWA program. In 2001, it was determined that the technology selection decision for the Pueblo and Blue Grass stockpiles would be a Defense Acquisition Board (DAB) decision. *An Overarching Integrated Product Team (OIPT) reported to the DAE the status of the Chemical Demilitarization Program and whether the ACWA technologies could meet the certification requirements and the findings of the Pueblo and Blue Grass Final EIS. The DAE considered all the information presented, including input from the affected communities, and documented and confirmed the resulting DAB selection in an Acquisition Decision Memorandum for each site. The DAB designated neutralization followed by biotreatment as the preferred alternative at Pueblo. The following identifies and describes the actions taken during each step.*

- **Removing the Energetics:** Robotic equipment will remove the weapon's energetic components, including the fuse and the burster.

- **Removing the Mustard Agent:** To remove the chemical agent, the body is mechanically accessed and then the agent is washed out with pressurized water.

- **Neutralizing the Energetics and Mustard Agent:** After the energetics and chemical agent have been separated from the metal parts, they will be treated in separate tanks with a caustic solution and water, respectively. The by-product from this process is called hydrolysate. The energetic hydrolysate and chemical agent hydrolysate are then combined and further processed.

- **Biotreatment:** The hydrolysates will go through the biotreatment process, which consists of large tanks containing microbes that digest and further break down the solution. Water released from the process will be recycled, leaving various salts and biosludge. Biosludge, which is made up of microbe waste products and other bacterial matter, will be filtered to remove water and shipped off-site to a permitted treatment, storage and disposal facility.

- **Disposing of the Metal Parts:** Although the metal parts were cleansed of energetics and chemical agent at the beginning of the process, they still may contain energetics and agent and need to be decontaminated to a higher level. This level is called "5X," a military standard of decontamination that ensures the metal is clean and safe for disposal. To reach this level of decontamination, the metal parts will be heated to 1,000 degrees Fahrenheit for a minimum of 15 minutes. The metal can then be recycled.

The DAB designated neutralization followed by supercritical water oxidation (SCWO) as the preferred alternative for Blue Grass. Below is a description of neutralization followed by SCWO:

- **Removing the Chemical Agents and Energetics:** Munitions are disassembled by modified reverse assembly. Chemical agent and energetics are separated.

- **Neutralizing the Chemical Agents and Energetics:** Chemical agent and energetics are chemically decomposed and neutralized by caustic or water hydrolysis. The resulting chemical compounds are known as hydrolysates.

- **Supercritical Water Oxidation:** The chemical agent and energetic hydrolysates are destroyed using SCWO units. SCWO subjects the hydrolysate to very high temperatures and pressures, breaking them down into primarily carbon dioxide, water and salts.

- **Treating the Metal Parts and Solid Effluents:** Metal parts are thermally decontaminated by heating to 1,000 degrees Fahrenheit for a minimum of 15 minutes. Solid effluents are recycled or tested prior to disposal in permitted landfills. Gas effluents are recycled or filtered before released to the atmosphere.

The final activity necessary to ensure that an alternative technology would be implemented involved preparation for acquisition of a pilot plant facility. PMACWA issued a Request for Proposal for a Pueblo systems contractor on July 17, 2002, and subsequently awarded the contract during the following September; a Request for Proposal for Blue Grass was issued on February 28, 2003 and awarded on June 13, 2003.

THE FUTURE

PMACWA met its initial mandate from Congress by ultimately demonstrating six technologies in less than five years after the program was created. With this mission accomplished, PMACWA is looking towards the future and has moved into the implementation phase. In light of this shift, PMACWA has changed its name to Program Manager Assembled Chemical Weapons Alternatives, to better reflect its evolving mission. However, despite this changing mission, the program is committed to its approach to active, open public participation.

PMACWA regards public participation as a critical key to its past and future successes. From its inception, the program has established a new standard for the degree of openness and coordination with affected local communities and stakeholders. When the Dialogue process began, the Colorado and Kentucky Citizens' Advisory Commissions and community groups were divided regarding the path forward. Over the course of the process, the Colorado community, including the CAC and more than 30 other major groups unanimously supported neutralization followed by biotreatment at their site. At the start of the Dialogue process in Kentucky, a CAC member noted that his community was "at absolute stalemate." After working through the Dialogue, the Kentucky CAC is in favor of PMACWA and the agency's preferred alternative for the disposal of chemical weapons at the Blue Grass Army Depot. Today, PMACWA is continuing to encourage public involvement through the development of community forums in both Kentucky and Colorado. Local residents and other stakeholders will continue to have a voice in decisions made about plans for chemical weapons disposal in their communities.

"We accomplished our mission through partnership, partnership with the government, the military and the public," said Parker. "I think that speaks volumes, not only for our approach, but also for the future."

ECONOMICAL DELIVERY OF DISSOLVED ORGANIC CARBON FROM PEAT AND WASTE WOOD PRODUCTS FOR USE AS ELECTRON DONORS

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PROBLEM STATEMENT

In order to plate or paint metal, it must be free from dirt and grease. Numerous solvents and procedures have been developed to accomplish this task. For many years, flammable solvents were employed to clean metal. While flammable solvents worked they presented fire, safety, and health concerns that eventually became unacceptable. Chlorinated solvents like trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA) were developed to overcome fire concerns and were employed for decades as degreasing agents. Leaks, spills, and past industrial disposal practices of chlorinated hydrocarbons have left a legacy of groundwater contamination. Several engineering approaches have been developed to remove chlorinated solvents from groundwater such as mechanical pump and treat systems, but most of these have been very expensive to start and operate. These short-comings inspired microbiologists and geochemists to investigate other remedial approaches.

Geochemists and microbiologists have found that most chlorinated solvent plumes can undergo reductive dechlorination in anaerobic environments. The bioremediation of these plumes requires a source of carbon to serve as electron donors and appropriate nutrient conditions (Chapelle 2001). These sources of carbon can exist in many different physical forms and chemical compositions. Recently, several approaches have been taken to enhance *in-situ* bioremediation of chlorinated solvents in aerobic aquifers through the delivery of various electron donors such as wood mulch, vegetable oil, molasses, lactate, and polylactate esters (ITRC 1998, Magar et al. 2001). The problem to date has not been the lack of suitable electron donors but their sustained and economical delivery to the subsurface. Delivery of electron donors usually entails injection, drilling, trenching, or some other mechanical disturbance of the subsurface. Existing delivery methods are often subject to biofouling and a limited range of influence due to subsurface heterogeneity. Field experiments with biobarriers consisting of wood mulch have been established at several sites in America with TCE contaminated groundwater. The results of these wood barriers have been promising. What is needed most is a method to deliver inexpensive and sustainable electrons like peat and wood mulch to the subsurface with minimal mechanical alteration. Is it possible to deliver

enough electron donors derived from either peat or mulch to promote reductive dechlorination without trenching or other anthropogenic subsurface intervention? The answer to this question may come from studies on waste wood covers employed in the remediation of uranium mining wastes in Ontario and Quebec, Canada conducted by (Tasse et al 1997) and (Reardon et al. 1984). Both Reardon and Tasse and Germain found that deposits of fine woods chips were able to generate enough dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) to promote anaerobic conditions at depths greater than 50 cm and influence the geochemistry of the underlying groundwater.

„Technical Maturity”

The study of humic substances is a century old scientific activity with regard to soil chemistry. In the past twenty years, research on humic substances in aquatic systems has provided a much better understanding of the chemistry and ecological significance of these substances.

Tranvik and Bertilsson (2001) studied the net effect of UV irradiation on DOC bioavailability and report that old humic material supports increased bacterial growth upon UV exposure. The emplacement of peat in ponds is anticipated to capitalize on these photodegradation processes and provide a bioavailable form of DOC to the underlying aquifer during periods of recharge. Although the DOC in peat soils may or may not benefit from photodegradation processes, Lorah et al. (1997) observed methanogenic conditions and the disappearance of TCE across a thin (approximately 6 feet) unit of peat at Aberdeen Proving Ground, Maryland. The emplacement of a layer of peat / peat soil in topographic depressions is anticipated to capitalize on similar processes. Fujii et al. (1998) report concentrations of DOC in peat soils ranging from 46.4 to 83.2 milligrams/liter (mg/L). These concentrations are well in excess of the DOC concentrations (1.6 to 1.8 mg/L) that were observed to support in-situ reductive dechlorination of TCE at a phytoremediation site within the plume proposed for study (Eberts et al. 2002); background concentrations of DOC in the Terrace Alluvial aquifer at the Carswell Phytoremediation Site, where no biodegradation is observed, range from 0.9 to 1.1 mg/L.

Additional bench scale and field scale evidence exists for the viability of using peat for remediation of chlorinated solvents. At the bench scale, Kao and Lei (2000) report that one half gram of peat has the potential to convert 1.5 mg of perchloroethylene (PCE) to ethylene. At the field scale, Buss et al. report that VOC concentrations in a chlorinated solvent plume were decreased from 100,000 ug/L to less than 10 ug/L after traveling a distance of less than 350 feet through peat rich subsurface. In addition, Bradley et al. (1998) observed that humic acids can also act as electron acceptors for the anaerobic microbial oxidation of DCE and VC. These researchers conclude that in the presence of humic acids, efficient mineralization of VC without the accumulation of reduced intermediates can occur.

The subsurface transport of DOC in relation to rain events also has been studied. Jardine et al. (1990) concluded that a significant flux of DOC through the subsur-

face environment during storm events can be expected. Winter (1995) notes that ground water recharge is highly variable and is initially focused where the vadose zone is thin, particularly near surface water bodies.

It is anticipated that it is possible to economically deliver DOC to an underlying aquifer by combining what is known about the ability of peat to promote biodegradation of TCE with what is known about ground water recharge and event driven DOC flux into the subsurface. The proposed study will document to what extent the emplacement of peat in ponds and / or topographic depressions can support the in-situ biodegradation of chlorinated solvents in an initially aerobic aquifer.

PROJECT DESCRIPTION

A possible technology solution is the combined use of peat or wood mulch and the natural or existing hydrologic / topographic setting to deliver sustained, inexpensive, and readily bioavailable dissolved organic carbon (DOC) to a shallow (less than 10 feet below ground surface) trichloroethylene (TCE) contaminated aquifer, and to serve as a source of electron donors for *in-situ* biodegradation of the TCE. Applications of the use of peat and mulch to increase the DOC in the underlying aquifer need to be investigated. For example sphagnum peat or wood mulch could be placed in the bottom of a pond and, in the other instance, sphagnum peat (or peat soil) will be placed in a topographic depression where water ponds in response to storm events. The purpose of the peat or wood mulch emplacement in each of these settings is to carry DOC enriched recharge to the contaminated aquifer during and immediately after periods of precipitation. This technology is innovative because it is a passive technology that capitalizes on the natural / existing hydrologic and topographic setting of a selected site and requires no operation or maintenance costs after initial peat emplacement; this is desirable for the long-term delivery of DOC to a contaminated aquifer. A team comprised of hydrologists, geochemists, and microbiologists would then monitor concentrations of DOC in the shallow ground water upgradient, beneath, and down gradient of the emplaced peat or mulch. This team would study associated effects on microbial communities that degrade chlorinated solvents. The affect of peat and mulch photodegradation products of peat humic substances, typically low molecular weight organic acids, on the formation of TCE daughter products (dichloroethylene (DCE), vinyl chloride (VC), and ethane and the consumption or production of geochemical indicators of *in-situ* biodegradation (dissolved oxygen, nitrate, ferrous iron, sulfate, sulfide, methane, carbon dioxide and dissolved molecular hydrogen) in the aquifer also will be determined.

Technical description

Sphagnum peat could be placed in the bottom of any existing pond located above a TCE ground-water plume. In addition, sphagnum peat / peat soil or wood mulch will be placed in a topographic depression where water ponds in response to storm events above the same plume. Grass will be planted

over the peat soil in the topographic depression to prevent the loss of the peat during periods of overland flow associated with storm events, as well as to minimize interference with golf course operation. These two sites, as well as a control pond and a control topographic depression in which no peat is emplaced, will be monitored for changes in DOC in the pore water of the pond sediments and in the aquifer. Samples for analysis of DOC in the pore water of the pond sediments will be collected by squeezing water out of sediment samples scooped from the bottom of the ponds. Samples for DOC in the aquifer upgradient and down gradient of the ponds will be collected from a line of well nests located parallel to the direction of ground water flow at each site. Samples for DOC in the aquifer upgradient, beneath, and down gradient of the selected topographic depressions also will be collected from a line of well nests located parallel to the direction of ground water flow at each of these sites. Samples for analysis of volatile organic compounds (VOCs), including TCE, DCE, VC, and ethene, and dissolved oxygen in the pore water of the pond sediments will be collected by use of water-diffusion samplers that will be buried in the sediments (<http://ds.itrcweb.org/common> accessed March 14, 2002).

Samples for analysis of VOCs, geochemical indicators of in-situ biodegradation, and a conservative tracer such as chloride will be collected from all wells using traditional well-purging techniques. Samples for determination of microbial ecology will be collected from sediment core. An analytical solute transport model, such as BIOCHLOR (Aziz et al. 2000), will be used to compute biodegradation rates for each sampling event. Water samples will be collected once prior to peat emplacement and four times per year for two years following peat emplacement. Three sampling events per year will be associated with precipitation events. One sampling event per year will take place during an extended dry period. A precipitation gage, soil tensiometers, pond stage gages, and pressure transducers in selected wells, including the well nests, will be used to help identify ground-water recharge events and determine the timing of sampling. Sediment core samples for determination of microbial activity will be collected once prior to peat emplacement and twice during the second year of the project. One of these sampling events will occur during a wet season and one will occur during an extended dry period. Samples of sediment core will be collected from coreholes drilled upgradient and down gradient of each site for the purpose of sediment sampling. Physical properties of the pond sediments and vadose zone sediments beneath the topographic depressions will be characterized prior to peat emplacement to aid in technology transfer. Such properties affect the ability of DOC enriched pond water or precipitation to reach the water table. Specifically, core will be collected from the pond sediments and analyzed in the laboratory for determination of vertical hydraulic conductivity. The grain-size distribution of core from beneath the selected topographic depressions will be determined for classification of the vadose zone soils. Water levels in each well and the stage of the pond will be recorded during each sampling event to record the depth to ground water and hydraulic gradient across each site.

Potential issues of concern and technical risks in taking the technology from the lab to the field

It is anticipated that minimal technical risks will be presented by taking this technology from the lab to the field. One potential concern is that excessive placement of peat into existing ponds may compromise the dissolved oxygen levels enough to impact the fish present. Other technical concerns are that not all waste wood products and mulch decay at the same rate. Some woods for example cedars (*Juniperus virginiana*), redwoods (*Sequoia sempervirens*), and osage orange (*Maclura pomifera*) are very resistant to decay and may not provide the amount of electron donors needed to promote reductive dechlorination.

Approach for determining performance and expected cost of the technology

The hydrological and geochemical data from a demonstration could be incorporated into a 2-D solute transport model, such as BIOCHLOR, to quantify changes in *in-situ* biodegradation rate constants that can be attributed to the emplaced peat. Changes in the distance of stabilization of the plume that can be attributed to the emplaced peat also will be calculated using the method of Chapelle and Bradley (1998). A 2-D ground water flow model, such as MODFLOW (McDonald and Harbaugh 1998), may be used to estimate the amount of

ground water recharge received at each site during the two year period of demonstration. There are minimal costs associated with this technology. It is expected that the peat will cost no more than \$ 1,000 per acre. The labor associated with peat emplacement is also estimated at \$ 1,000 per acre. No operation and maintenance costs are anticipated once the peat or mulch is in place.

EXPECTED BENEFIT

Persistent plumes of chlorinated solvents are an enormous liability to owners of industrial sites with groundwater with chlorinated solvents. The economical delivery of sustained electron donors to the subsurface zone has proven problematic. If it is possible to deploy readily available and inexpensive peat humic substances or waste wood products such as mulch to provide a source of carbon and electron donors to groundwater discharge/recharge areas via ponds and existing topographical drainage features, a low technology, then a passive affordable method will be available to remedial project managers. Both mulch and peat are commercially available, easy to handle, and widely accepted by both the public and other parties. It may also be possible to deliver DOC to the subsurface from other sources of cheap carbon, such as grass clippings or agricultural wastes, in a similar fashion.

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