Environmentally sound management (ESM) practices on cleaning up obsolete stockpiles of pesticides for Central European and EECCA Countries

PROCEEDINGS

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<td>M.Sc. Leon Urlings, The Netherlands</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS

**PREFACE**  
Prof. Ivan Atanassov and John Vijgen ................................................................. 10

**INTRODUCTION**  
Prof. Ivan Atanassov and John Vijgen ........................................................................ 11

**OFFICIAL STATEMENTS AND SOFIA DECLARATION**

**WELCOME SPEECHES**  
*Prof. Ivan Atanassov* .......................................................................................................................... 13
*Dr. Borislav Velikov* ............................................................................................................................... 14
*Mrs. Dolores Arsenova* ........................................................................................................................... 14
*John Vijgen* ........................................................................................................................................... 15
*Prof. Konstantin Terytze* ....................................................................................................................... 16
*Roland Wiederkehr* ................................................................................................................................. 17

**CLOSURE SPEECHES**  
*Dan Jorgensen* ................................................................................................................................. 17
*Bart Staes* .............................................................................................................................................. 18
*Stavros Dimas* ......................................................................................................................................... 18
*Mugur Cracian* ....................................................................................................................................... 19
*Archalus Tcheknavorian* ....................................................................................................................... 19
*Roland Wiederkehr* ................................................................................................................................. 20

**SPECIAL LETTER**  
*Wieslaw Kuc* ....................................................................................................................................... 21

**DECLARATION OF THE 8th INTERNATIONAL HCH AND PESTICIDES FORUM** ...................... 22

**GEORGIAN EXHIBITION ON OBSOLETE PESTICIDES**  
*Otar Kiria: Explanation and photos* .................................................................................................. 26

**THEME I: STATE OF OBSOLETE PESTICIDES IN CENTRAL/EASTERN EUROPE, CAUCASUS REPUBLICS AND CENTRAL ASIA REPUBLICS**

**ORAL PRESENTATIONS**  
ENVIRONMENTALLY SOUND MANAGEMENT, APPROACHES AND CONTROL OF OBSOLETE & POPS PESTICIDES IN BULGARIA  
*Manuela Georgieva* .............................................................................................................................. 27

DANISH SUPPORT ON ENVIRONMENTALLY SOUND MANAGEMENT OF OBSOLETE PESTICIDE. ACAP ACTIVITIES IN RUSSIA  
*Mikala Klint* .......................................................................................................................................... 28

DEALING WITH OBSOLETE PESTICIDE’S HAZARDS IN ARMENIA  
*E. Manvelyan, L. Simonyan, E. Anakhasyan* ............................................................................................ 30

MANAGEMENT OF OBSOLETE PESTICIDES IN THE REPUBLIC OF MOLDOVA  
*Iurii Malanciuc, S. Stasiev, A. Veleva, C. Mogoreanu* ............................................................................. 32

AN ATTEMPT AT RECORDING OBSOLETE PHYTOPHARMACEUTICAL SUBSTANCES IN THE REPUBLIC OF SLOVENIA  
*B. Druzina, M Ciraj, V. Terni, Z. Bolta, V. Skerlavaj, H. Leskovsek-Sefman* ......................................... 36

THE STATE OF OBSOLETE PESTICIDES IN UZBEKISTAN  
*Narian Umarov, Zulfia Saleimanova* ....................................................................................................... 40
IMPLEMENTING STOCKHOLM CONVENTION NATIONAL PLANS: WAYS FORWARD

David Piper ...................................................................................................................................................................... 41

МОРНОРИНГ ЗАПРЕЩЕННЫХ И НЕПРИГОДНЫХ К УПОТРЕБЛЕНИЮ ПЕСТИЦИДОВ

РЕСПУБЛИКЕ БОЛГАРИИ
Пётр Николов.................................................................................................................................................................. 47

DEVELOPMENT OF NIP FOR THE IMPLEMENTATION OF STOCKHOLM CONVENTION ON POPS IN

GEORGIA
Givi Kalandadze ............................................................................................................................................................... 51

COPING WITH STOCKPILES OF OBSOLETE CROP PROTECTION PRODUCTS IN SLOVAKIA
Jozef Kotleba, Jaroslav Legath, Stanislav Barok, Jan Kolnik ................................................................................................ 53

ORGANOCHLORINATED PESTICIDES (OCPS) IN THE CZECH REPUBLIC. PART I. ASSESSMENT
OF THE HISTORICAL PRODUCTION, USE, IMPORT AND EXPORT AND OBSOLETE STOCKS
Ivan Holoubek, Jana Klánová, Jakub Hofman, Jiří Matoušek, Milan Sáňka, Radim Vácha, Jiří Zbíral,
Milan Matoušek ............................................................................................................................................................... 55

ORGANOCHLORINATED PESTICIDES (OCPS) IN THE CZECH REPUBLIC. PART II. OCCURRENCE
AND LEVELS IN AIR, WATER AND SOIL
Ivan Holoubek, Jana Klánová, Jakub Hofman, Petra Kosubová, Penka Shegunova, Milan Sáňka, Radim Vácha,
Jiří Zbíral ........................................................................................................................................................................... 60

ENVIRONMENTALLY SOUND MANAGEMENT OF STOCKS OF OBSOLETE PESTICIDES IN THE
RUSSIAN FEDERATION – AN ARCTIC COUNCIL ACTION PLAN (ACAP) PROJECT
T. Seppälä, E. Barnes, R. Dyer, J. Henttonen, M. Klimova ............................................................................................. 64

ANALYSIS OF THE CURRENT STATUS OF TREATMENT OF PROHIBITED AND OBSOLETE
PESTICIDES IN THE CONTEXT OF THE DEVELOPMENT OF THE NATIONAL PLAN FOR IMPLEMENTATION
OF THE STOCKHOLM CONVENTION ON PERSISTENT ORGANIC POLLUTANTS
Olena. V. Ligostayeva and A. Antonov ............................................................................................................................ 67

SUBMITTED PAPERS

PESTICIDES IN KAZAKHSTAN
Lidiya Astanina ................................................................................................................................................................ 71

INTENSIVE APPLICATION OF CHEMICALS – RESULTS ARE HARD TO UNDERESTIMATE
Olga Speranskaya ............................................................................................................................................................. 72

THE STATE OF OBSOLETE PESTICIDES IN BOSNIA & HERZEGOVINA
R. Numic, H. Custovic ...................................................................................................................................................... 73

THEME II: MONITORING AND ASSESSMENT OF CONTAMINATION BY OBSOLETE
PESTICIDES AND NGO’S POINTS OF VIEW

ORAL PRESENTATIONS

PCDD/PCDF CONTAMINATION FROM HISTORICAL PESTICIDE USE AND PRODUCTION – A CASE STUDY
USING DATA FROM JAPAN AND GERMANY
Roland Weber, Shišeki Masunaga ........................................................................................................................................ 75

HCH RESIDUES IN SOME FRESH WATER, SEDIMENT AND IN SOME AQUATIC ORGANISMS IN TURKEY
Durdane Kolankaya ............................................................................................................................................................. 81

BIOACCUMULATION OF ORGANOCHLORINE COMPOUNDS IN EGGS OF TESTUDO HERMANNI
BOETGERI (HERMAN’S TORTOISE) FROM THE IRON GATES NATURE PARK, ROMANIA
Marius Matache, M. Zaharia, C. Hura, L. Rozyłowicz ........................................................................................................ 86

PESTICIDES WATER CONTAMINATION IN BULGARIAN DANUBE REGION
Sela Stankova, Galia Bardarska ........................................................................................................................................... 89

EMISSION AND RESIDUE INVENTORIES FOR SELECTED ORGANOCHLORINE PESTICIDES AND
THEIR CONTRIBUTIONS TO THE ENVIRONMENTAL STUDY
Yi-Fan Li .............................................................................................................................................................................. 91

DEVELOPMENT OF CONDITIONS, ISSUES AND CAPACITY BUILDING NEEDS IN THE PESTICIDES
MANAGEMENT IN BULGARIA (THE POINT OF VIEW OF THE NGO’S ASSESSMENT)
Irina Iordanova .................................................................................................................................................................. 99

OBSELETE AND BANNED PESTICIDES IN UKRAINE: CURRENT STATE, RELATED PROBLEMS AND
ROLE OF EDUCATION
Valentina Pidlisnyuk, Tatyana Stefanovska ...................................................................................................................... 100
SUBMITTED PAPERS

DISTRIBUTION OF HCH-ISOMERS IN THE BALTIC HERRING OF THE ESTONIAN COASTAL SEA
Ott Roots, Antti Roose, Mart Simm ................................................................. 105

LINDANE IN THE BALTIC FISH IN THE ESTONIAN COAST OF THE BALTIC SEA
Ott Roots, T. Lukki .......................................................................................... 107

THEME III: WASTE TECHNOLOGIES

ORAL PRESENTATIONS

POLISH EXPERIENCE ON SITE REMEDIATION FOLLOWING REMOVAL OF UNDERGROUND
PESTICIDE STOCKS – LEGAL AND FEASIBILITY ASPECTS
Stanislaw Stobiecki, A. Silowiecki, I. Giza, K. Waleczek, T. Stobiecki ................................................................. 109

THE USE OF ALTERNATIVE TECHNOLOGIES FOR THE TREATMENT OF HAZARDOUS WASTES
Christophe Rittersberger .................................................................................. 114

THERMAL DESTRUCTION OF OBsolete PESTICIDES
Kaare Helge Karstensen .................................................................................... 118

METHOD FOR ECOLOGICAL UTILIZATION OF PESTICIDE RESOURCES WITH EXPIRED APPLICATION
TERM BY THERMAL DESTRUCTION IN COKING MODE OF THE COAL BLEND
Dimitar Dimitrov, Vasil Popov ......................................................................... 121

RELEVANCE OF PCDD/PCDF FORMATION FOR THE EVALUATION OF POPs/PESTICIDE DESTRUCTION
TECHNOLOGIES – CURRENT STATUS AND ASSESSMENT GAPS
Roland Weber ..................................................................................................... 124

THE APPLICATION OF COPPER MEDIATED DESTRUCTION METHOD (CMD) FOR DESTRUCTION OF
CHLORINATED PESTICIDES AND SOME PRE-DIOXIN AND POP COMPOUNDS
Pekárek Vladimir, Ocelka Tomas, Grabic R. ....................................................... 130

A GREEN OXIDATIVE APPROACH FOR RAPID TOTAL DEGRADATION OF THIOPHOSPHATE PESTICIDES
Terrence J. Collins, Arani Chanda, DeboShri Banerjee and Sushil Khetan ................................................................. 133

ADVANCES IN BCD TECHNOLOGY
John Fairweather .............................................................................................. 135

GPCR TECHNOLOGY AND VENDOR UPDATE
Craig McEwen, Dr. Douglas Hallett, Kelvin Campbell ....................................... 137

SUBMITTED PAPERS

ЭКОЛОГИЧЕСКИЕ ЭФФЕКТИВНОЕ УПРАВЛЕНИЕ ПЕСТИЦИДАМИ
Э. Мамедов, И. Бабаев ................................................................................... 139

THEME IV: SOIL AND WATER REMEDIATION

ORAL PRESENTATIONS

BIOCATALYTIC DECHLORINATION OF LINDANE BY NANOPARTICLES OF PD(0) DEPOSITED
ON SHEWANELLA ONEIDENSIS
Birgit Mertens, Christian Blothe, Kim Windey, Win De Windt and Willy Vertsraete ...................................................... 143

A SYNTHESIS AND A CRITICAL REVIEW ABOUT THE TREATMENT OF POLLUTED SITES WITH THE
HCH-ISOMERS
Estell Roth, B. Fabre, C. Dutheil ...................................................................... 145

UPTAKE AND TRANSLOCATION OF DDT IN NATIVE PLANTS AT A CONTAMINATED SITE IN CANADA
Barbara Zeeb, A. Lunney, A. Rutter, V. Bacher, & K. Reimer ................................................................. 148

INTRINSIC AND STIMULATED IN SITU BIODEGRADATION OF HEXACHLOROCYCLOHEXANE (HCH)
A. Langenhoff, Sjef Staps, C. PiJs, A. Varkevisser, R. Lassche, G. Zwiep ................................................................. 151

HEXACHLOROCYCLOHEXANE (HCH) RESIDUES IN INDIAN ENVIRONMENT: PROBLEMS AND SOLUTIONS
Rup Lal, Mandeep Dadihwal, Ajaib Singh, Om Prakash, Shweta Malhotra, Poonam Sharma ......................................... 154

USE OF WILD PLANTS FOR PHYTOREMEDITION OF KAZAKHSTAN SOILS POLLUTED WITH PESTICIDES
Asil Nurzhanova, Peter Kulakow, Ellen Rubin, I. Rakimbayev, A. Sedlovskiy, K. Zhambakin, S. Kalaugin,
L. Kalmykov, L. Erickson .................................................................................. 157
POSTER PRESENTATIONS
A GROUNDWATER TREATMENT PLANT FOR REMEDIATION OF DDT, HALOGENATED ORGANICS, ARSENIC AND MERCURY AT THE LAGO MAGGIORE (NORTH ITALY)
J. Prantner, U. Korherr, Roland Weber .......................................................................................................................... 160
TRANSFORMATION OF BETA- AND DELTA-HEXACHLOROCYCLOHEXANE BY SPHINGOMONAS PAUCIMOBILIS B90A
Vishakha Raina, Hans-Rudolf Buser, Christoph Holiger and Hans-Peter E. Kohler ................................................................. 163
DEVELOPMENT OF THE TECHNOLOGY FOR BIOREMEDIATION OF SOILS, CONTAMINATED BY TOXIC CHEMICAL COMPOUNDS WITH THE HELP OF MICROORGANISMS-DEGRADERS
G. A. Zharikov, R. V. Borovich, A. A. Leontievsky, I. I. Starovoitov .................................................................................. 165

SUBMITTED PAPERS
BIOTECHNOLOGICAL ASPECTS OF ECOLOGICALLY PURE PESTICIDE-FREE FOODSTUFF PRODUCTION
Tatiana A. Nugmanova .......................................................................................................................................................... 169

THEME V: HEALTH RISKS ASSESSMENT BY OBSOLETE PESTICIDES

ORAL PRESENTATIONS
SOIL-PLANT TRANSFER OF ORGANIC CHEMICALS AND DERIVATION OF TRIGGER VALUES
Konstantin Terytze, Werner Kördel, Josef Müller, M. Herrchen, A. Nestler.................................................................................. 171
PESTICIDE RESIDUES IN THE EGGS OF PEREGRINE FALCONS AND OTHER WILD BIRD SPECIES IN BADEN – WUERTTEMBERG – PRESENT STATE AND TIME TREND
Karl Theo von der Trenck, F. Baum, H. Hartwig, R. Malisch, F. Schilling, R.-D. Zimmermann .................................................................. 175
TOXICITY OF PESTICIDES IN THE PRESENCE OF HEAVY METALS ON BIOCHEMICAL OXIDATION OF AMMONIA IONS
Maria Sandu ........................................................................................................................................................................... 179
ELIMINATION OF ACUTE RISKS OF OBSOLETE PESTICIDES IN MOLDOVA, ARMENIA AND GEORGIA
Willem Tjebbe Oostenbrink ...................................................................................................................................................... 181
APPLICATIONS OF SPMDs AS A TOOL FOR ASSESSMENT OF PESTICIDES AND OTHER PERSISTENT ORGANIC POLLUTANTS IN WATER
Ocelka Tomas, Grabic R., Koci V. ........................................................................................................................................... 185

POSTER PRESENTATIONS
ORGANOCHLORIDE PESTICIDES BLOOD LEVELS IN THE POPULATION OF CIDADE DOS MENINOS, DUQUE DE CAXIAS COUNTY, RJ, BRAZIL: PRELIMINARY RESULTS
R.J. Koifman, P.N. Sarcinelli, A C. S. Rosa, I.E. Mattos, I.A.M Castilho, S. Koifman ........................................................................ 189

SUBMITTED PAPERS
HEALTH EFFECTS OF PESTICIDE APPLICATION
D. Dumanyan, Hmayak Avagyan .................................................................................................................................................. 191

THEME VI: WASTE MANAGEMENT

ORAL PRESENTATIONS
DEVELOPMENTS ON TECHNICAL GUIDELINES ON OBSOLETE PESTICIDES MANAGEMENT
Mark Davis ................................................................................................................................................................................... 193
OBSOLETE PESTICIDES MANAGEMENT IN UKRAINE, BELARUS AND RUSSIA
Joern Lauridsen ........................................................................................................................................................................... 195
MANAGEMENT OF OBSOLETE PESTICIDE CLEANUP IN ROMANIA
Neel Stroebaek ........................................................................................................................................................................... 197
MANAGEMENT OF OBSOLETE STOCKS: THE INNOVATIVE OBSOLETE PESTICIDES MANAGEMENT PROGRAM WIM
Jan Betlem ................................................................................................................................................................................... 198
OBSOLETE PESTICIDE DISPOSAL PROJECT IN ETHIOPIA
Pasi Silvennoinen ........................................................................................................................................................................... 200
PREFACE

This book titled “Environmentally sound management (ESM) practices on cleaning up obsolete stockpiles of pesticides for Central European and EECCA Countries” contains selected presentations of the 8th International HCH and Pesticides Forum, (26 -28 May, Sofia, Bulgaria).

The Forum was organized along six main themes:
1. State of Obsolete Pesticides in Central/Eastern Europe, Caucasus Republics and Central Asia Republics
2. Monitoring and assessment of contamination by obsolete pesticides and NGO’s points of view
3. Waste Technologies
4. Soil and Water Remediation
5. Health risks assessment by obsolete pesticides
6. Waste Management

These items are discussed in a number of oral and poster presentations and supplemented with submitted papers and arranged accordingly within the framework of the themes. As an introduction to the Forum, welcome and closure speeches are included. A short “Sofia Declaration” which was accepted by all participants mutually is presented also. To keep up with the fast developments in the field of environmentally sound management of obsolete pesticides, the organisers of the 8th International HCH and Pesticides Forum decided to publish the proceedings as fast as possible.

Therefore the contributions have been reviewed scientifically from the Scientific Committee of the 8th International HCH and Pesticides Forum and after some editorial work to avoid possible orthographic errors, have been copied directly from the manuscripts.

The organizers of the 8th International HCH and Pesticides Forum and editors would like to express their acknowledgement to the authors for their prompt replies, which enabled to prepare and publish this book on a comparatively short term.

We would like to express our gratitude for the support we received in the organization of the 8th International HCH and Pesticides Forum and proceedings from:

Ministry of Environment and Waters of Bulgaria
International HCH & Pesticides Association (IHPA), The Netherlands
National Center for Agricultural Science, Sofia, Bulgaria
Institute for Sustainable Development, Sofia, Bulgaria
Federal Environment Agency of Germany (UBA)
Committee of Environmental Protection to National Assembly of Bulgaria
Ministry of Agriculture and Forestry, Bulgaria
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Department for Environment Food and Rural Affairs, Defra, United Kingdom
Swiss Agency for Development Cooperation, SDC, Switzerland
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Tauw Group, The Netherlands
Orel – G. Holding Ltd., Bulgaria

Ivan Atanassov, John Vijgen
INTRODUCTION

ENVIRONMENTALLY SOUND MANAGEMENT PRACTICES ON CLEANING UP OBSOLETE STOCKPILES OF PESTICIDES FOR CENTRAL AND EASTERN EUROPE, CAUCASUS AND CENTRAL ASIA COUNTRIES

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Bulgaria

John Vijgen – IHPA
The Netherlands

According to current investigations, the amount of obsolete pesticides in Central and Eastern European Countries, together with the states in the Central Asia region is estimated to be at least several hundred thousand tons. It is accepted, that the amount of obsolete pesticides in Balkan Countries is more than 45 000 tons. Especially in Bulgaria, these substances are more than 12500 tons, distributed between 1800 warehouses, spread all over the country.

These hazardous chemicals have been used in large quantities in the past and they still persist in the environmental media and adversely affect population and ecosystems. Most of the abovementioned countries have band production, use and import of these chemicals, but still now there are large amounts of stockpiles which have to be handled safely and eliminated using environmentally sound technologies.Obsolete pesticides fall within the scope of the Stockholm Convention on Persistent Organic Pollutants (2001), entering into force on 17th of May 2004. Many of the Countries in Central and Eastern Europe, as well as the countries in Caucasus and Central Asia region are parties to the Stockholm Convention and have declared their intention to ratify and implement the Convention through development of national inventories, action plans and strategies required under Convention. This is the only way to support the integrated approach in elimination the obsolete pesticides stockpiles and environment protection policy and to bridge the still existing gap between science and policy in this field.

The Forum, therefore, had two main aims:

• To present the state-of-the-art of research, national inventories, action plans and environmentally sound technologies on cleaning up obsolete stockpiles of pesticides in Countries from Central and Eastern Europe, Caucasus and Central Asia region;
• To bring together scientists, administrators, policymakers, business people and NGO’s working on problems of obsolete stockpiles of pesticides in order to catalyze efforts towards implementation of Stockholm Convention on POPs and eliminate the hazards coming from obsolete pesticides.

To reach these two main aims the Forum was organized in six themes: (1) State of obsolete pesticides in Central/Eastern Europe, Caucasus Republics and Central Asia Countries; 2) Monitoring and assessment of contamination by obsolete pesticides and NGO’s points of view; (3) Waste technologies; (4) Soil and Water remediation; (5) Health risk assessment by obsolete pesticides; and (6) Waste management. Each theme was discussed in plenary sessions and workshops.

The First theme: “State of obsolete pesticides in Central/Eastern Europe, Caucasus Republics and Central Asia Countries” was intended to describe the situation with obsolete pesticides in different Countries and outline the national approaches to solve the problem in the frame of Stockholm Convention on POPs. In relation to this theme, presentations of Peter Nikolov (Bulgaria), Ivan Holoubek et al (Czech Republic), Olena Ligostayeva and Anatoliyi Antonov (Ukraine) and others have to be mentioned. Further, within this theme the basic concepts of Council of Europe and different European and international organizations were presented by David Piper (UNEP), Dan Jorgensen and Bart Staes (EU Parliament).

The second theme: “Monitoring and assessment of Contamination by obsolete pesticides and NGO’s points of view” contained a deep going discussion on the concepts of obsolete pesticides monitoring, analysis and procedures for assessment of pollution of soils, waters, plants and other organisms by pesticides. Keynotes were presented on these aspects by Roland Weber (Germany), Irina Iordanova (Bulgaria) and Durdane Kolankaya (Turkey).

The third theme: “Waste technologies” concentrated on the different approaches and methods for destruction, utilization and safety storage of obsolete pesticides. Keynotes on issues were presented by Stanislaw Stobiecki et al (Poland), Christophe Rittersberger (France), Kaare Helge Karstensen (Norway), Terrence Collins et al (USA).

The fourth theme: “Soil and water remediation” illustrated mainly bio/phytotechnologies, which can be used as an effective tool for remediation of polluted soils and waters. This was illustrated by keynotes of Estelle Roth (France), Barbara Zeeb (Canada) and the review of Asil Nurzhanova (Kazakhstan) and Peter Kulakov (USA).

The fifth theme: “Health risk assessment by obsolete pesticides” clearly revealed the difficulties in setting soil/water quality standards and their implementation for health risk assessment in case of pollution by obsolete pesticides. A method for setting soil trigger values for POPs based on soil-plant transfer of organic chemicals was presented by Konstantin Tertyze, Werner Kördel and Josef Müller (Germany). A method for assessment the organic pollution in water was pre-
sented by Tomas Ocelka et al (Czech Republic).

The sixth theme: “Waste management” finally illustrated that waste pesticides management and waste treatment also provide possibilities for profitable activities. This primarily deals with collection of obsolete pesticides, their disposal, safety storage and destruction. The implementation of these procedures is restricted by lack of finance; lack of technical capacity in affected countries by obsolete pesticide stockpiles, resistance the problems of obsolete pesticides to be prioritised and the lack of public awareness. Keynotes on these issues were presented by Mark Davis (FAO), Robert Denny (USA), Jörn Lauridsen (Denmark).

A concise descriptions of the problems with obsolete pesticides stockpiles in affected countries and recommendation how to solve them contains the “Sofia Declaration”, accepted in the 8th Forum. This declaration, as well as the materials presented in the book will be assessed as contribution for the creation of an effective strategy for elimination of the hazards coming from obsolete pesticides in Central and Eastern Europe, Caucasus and Central Asia Countries.
OPENING ADDRESS

Prof. Ivan Atanassov
Chairman of the Organizing Committee of the 8th International HCH and Pesticides Forum

Dear participants,
Distinguished guests,
Ladies and Gentlemen,

Allow me, on behalf of the Organizing Committee to welcome all of you to the 8th International HCH and Pesticides Forum.

The purpose of the Forum is to continue the discussion, which began in Kiev (2003) for creating a program for environmentally sound management (ESM) of obsolete pesticides and other stocks of unwanted persistent organic pollutants (POPs) for Central and Eastern Europe, the Caucasus and Central Asian countries.

Obsolete pesticides pose a serious threat to human health and environment and are considered under the Stockholm Convention on Persistent Organic Pollutants as hazardous waste. Parties to the Stockholm Convention have the obligation to develop a National Implementation Plan including inventory and elimination of POPs waste. In accordance with the Stockholm Convention, the scope of the Forum can be defined as follows:

– To review past and ongoing activities related to ESM of obsolete pesticides in Central and Eastern Europe, the Caucasus and Central Asia;
– To develop recommendations for working network for these countries;
– To discuss technologies for safety storage/elimination of the obsolete pesticides;
– To discuss policy considerations and strategies for elimination of obsolete pesticides.

These issues are discussed in the presented 82 oral and poster reports, which as a whole cover the planned topics.

The contributions describe the situation with obsolete Pesticides in the separate countries and treat the issues connected with monitoring and assessment of contamination by obsolete pesticides, waste technologies, soil and water remediation technologies, health risks assessment and finally - the policy considerations to start-up the process of elimination of obsolete pesticides and improvement of the environment in Central and Eastern Europe.

I hope that the presented articles can be considered as a real contribution for solution of the issues with obsolete pesticides. All presented papers will be published in a special edition.

The Forum is organized by the International HCH and Pesticides Association, the Ministry of Environment and Waters of Bulgaria, the National Center for Agricultural Science – Bulgaria, the Institute for Sustainable Development – Bulgaria and the Federal Environment Agency - Germany with the support of BalBok engineering – Bulgaria, European Crop Protection Association (ECPA), the Federal Ministry of Agriculture Forestry, Environment and Water Management - Austria, the Department for Environment Food and Rural Affairs (UK), Swiss Agency for Development Cooperation (SDC), Ramboll-Denmark, Tauw Group – The Netherlands, Orel G. Holding – Bulgaria. Also it is necessary to note the successful cooperation with the National Agency of Plant Protection and the Sunny Days Foundation – Bulgaria. On behalf of the Organizing Committee I would like to thank these organizations for their help and financial support.

I want to express my gratitude to the members of the Local Organizing Committee and the authorities of the Ministry of Environment and Waters who contributed significantly to the organization of the 8th International HCH and Pesticides Forum. I have to stress the leading role of the National Assembly of Republic of Bulgaria to start-up the process of preparation and continual support of the activities connected with organization of the Forum.

I wish to thank personally to Mr. John Vijgen, director of the International HCH and Pesticides Association for his endeavors in organizing this meeting and for choosing Bulgaria as a host country of the Forum.

More than 130 participants from 40 countries take part in this Forum. Among them representatives from Central and Eastern Europe, the Caucasus and Central Asia, as well as from countries in Western Europe, America and Africa. The main distinguishing feature of the Forum is the attendance of participants with different responsibilities: scientists (in various fields: environment, agronomy, medicine, economy, environment technologies), political leaders (government members, parliament members, administrators), members of civil society (NGO, managers) representatives of companies and business. I would like to stress the participation of representatives from the European Parliament, FAO, the World Bank and UN. I hope that this will be a good base for comprehensive scientific and political discussions on the issues connected with the elimination of the threats posed by waste pesticides.

Ladies and Gentlemen,

After these remarks allow me to declare on behalf of the Organizing Committee the 8th International HCH and Pesticides Forum open. I wish the Forum to be successful and useful.

Sofia, 26.05.2005
H. E. Mr. Borislav Velikov  
President of the National Assembly,  
Republic of Bulgaria

Mrs. Arssenova,  
Distinguished Delegates,  
Ladies and Gentlemen,

It is my honour and pleasure on behalf of the Bulgarian National Assembly to welcome all of you, representatives of national and international governmental and non-governmental organizations to in the 8th International HCH and Pesticides Forum in Sofia.

The fact that the Forum is held in Sofia with a great international participation is an indicator for its significance and for the active participation of Bulgaria in the efforts of the European Community to solve the problems with the Persistent Organic Pollutants (POPs).

The topics to be discussed at the Forum are of vital significance because of their impact upon the environment, upon the quality of life and our health.

Environmental protection attracts special public attention and I hope that the issues concerning obsolete pesticides, as well as other hazardous substances will receive efficient and sustainable solution.

In international aspect there are four significant dates in relation to the issues concerning Persistent Organic Pollutants:

– In May 1995 the Governing Council of the United Nations Environmental Programme (UNEP) took the decision for a global assessment of 12 (twelve) hazardous substances and preparations (Persistent Organic Pollutants), nine of which are the pesticides, Aldrin, Dieldrin, Hexachlorobenzene, Toxaphene, Mirex, Endrin, Chlordane, Polychlorinated Biphenyls, DDT, Heptachlor.

– In February 1997 the Governing Council of United Nations Environmental Programme (UNEP) took the decision to initiate international activities to prepare an international legally binding instrument on the twelve (12) Persistent Organic Pollutants (POPs).

– In May 2001 at the A Conference of Plenipotentiaries in Stockholm was adopted and opened for signing the Convention on the Persistent Organic Pollutants, the Stockholm Convention.

– In May 2004 the Stockholm Convention officially entered into force for the countries that ratified it.

The Convention is signed by 151 states. Bulgaria also signed the Convention in May 2001 at the Conference of the Plenipotentiaries in Stockholm. The Convention was ratified by the Bulgarian Parliament on the 30th September 2004 and in March 2005 it entered into force for our country.

The Parties to Convention are obliged to conduct policy and take measures to eliminate intentional production and use of Persistent Organic Pollutants, to ban the export and import of POPs and to restrict unintentionally produced POPs.

The practical steps taken by Bulgaria through the Ministry of Environment and Water are related to the development of a National Implementation Plan for the Management of Persistent Organic Pollutants. The Implementation Plan includes a set of measures to comply efficiently with the requirements of the Convention.

Ladies and gentlemen,
Let me wish you fruitful discussion, creative and inspiring meetings and setting directions for further actions in the field of obsolete pesticide disposal with sustainable environmental protection in mind.

Thank you for your attention!

H. E. Mrs. Dolores Arssenova  
Minister of Environment and Water,  
Republic of Bulgaria

Mr. Velikov,  
Distinguished Delegates,  
Ladies and Gentlemen,

It is my honour and pleasure to greet with welcome to the 8th International HCH and Pesticides Forum all of you – representatives of national and international governmental and non-governmental organisations.

The fact that the forum is held in Sofia is a proof of the active position and policy of our country in the solution of the issues concerning the environmentally sound management of Persistent Organic Pollutants.

I am convinced that this event will present excellent opportunities for discussion, knew knowledge, exchange of information and good practices in the field of safe storage of obsolete pesticides. In my capacity of Minister of Environment and Water, I would like to assure you that the Government of the Republic of Bulgaria takes responsibly its obligations for the implementation of the Stockholm Convention on Persistent Organic Pollutants and the team of the Ministry works dedicatedly and professionally for the realization of the main priorities in the field of environmental protection and remediation as well as for the improvement of the quality of life in Bulgaria.

Our country has already started the practical implementation of the requirements of the Convention:

– A National Implementation Plan for the Management of Persistent Organic Pollutants is being developed, which will be endorsed by a National Coordinating Committee which includes experts from different Ministries, Research Organisations, universities and non-governmental organizations;
– The Ministry of Environment and Water through the Enterprise for Management of Environmental Protection Activities annually allocates significant financial resources for the solution of the obsolete pesticides problems. Last year BGN 2 million were allocated for this purpose. These measures and activities show that the problem with the obsolete pesticides is clearly identified and our country is determined to continue to implement the necessary measures for full compliance with the requirements of the Stockholm Convention.

I am convinced, ladies and gentlemen, that today’s forum will give new incentives for the realization of this policy.

Ladies and gentlemen,
I wish successful and fruitful work to the 8th International HCH and Pesticides Forum.
Thank you for your attention!

John Vijgen
IHPA Director

May I first give a big compliment to the Minister of Environment and the Head of the Bulgarian Parliament to come here and to open the Forum in the beautiful Sofia – the Capital of Bulgaria.

A second compliment I must give to my dear friend Prof Atanassov, and his team Anna Balinova, Alexander Atanassov, Venelina Koleva, and also the people from the Ministry of Environment and Water and personally to Mr. Nikolai Kenanov and all other persons highly committed to host this event shall receive my sincere gratitude.

Then to the Forum and the days in front of us:

Firstly, I would like to address the ongoing discussion: Why we invite politicians in a technical Forum?

I fully understand that the question is put forward, but the history of the IHPI has proven that it is necessary. Why?

We have learned that scientists alone cannot solve the problems of obsolete pesticides!

We came to this conclusion in 2001 – after the first 10 years of the Forum. Therefore we aimed at trying to convince dedicated politicians on the urgency of the obsolete pesticides problem, and with the help of the politicians we might be able to go beyond nice paper talk at start working on solutions and the fundraising for the necessary financial support.

And even though, we have this time been confronted with the very late canceling of 2 MEPs, they are still willing to send us a message. And not only from them, also the EU Commissioner for Environment Mr. Dimas sends his warmest regards to us all.

Secondly, How far are we in the Region with the solutions of obsolete pesticides?

Our strong appeal for an International Program for the Region to clean up as we discussed at the end of the 7th Forum in Kiev was not supported during our efforts during the last 2-3 years.

Even though the African Stockpile Program will be started eventually, I believe that the International society is not willing such kind of programs. However the possibilities we see is in the regional networking and exchanges of training programmes.

But what is then possible?

There are 3 main strategies, which can lead to success:

• The EU Accession and EU New Neighbor structure and corresponding funding programs may offer solutions, some short term others long term.

Several years of intensive discussions and correspondence with the EU Commissioner for Environment concluded the above said as regards a dedicated International Program. But the EU Commissioner stated very clearly that those countries that request and set the issue of Obsolete Pesticides, as a high priority will be helped!

Albania did so. Romania did so... and Moldova is on the way to get a World Bank project, but is still looking for co-financing.

Bulgaria should be able to obtain support within the PHARE Program. Ukraine – the biggest problem owner in the region - has not received any substantial help yet.

• The second strategy is the use of the Stockholm Convention. This is the right mechanism to address the problems and only countries that are able to use the funds for the National Implementation Plans optimal can be successful. Not the production of a huge pile of papers is the goal, but going into the field and finding out what is really at stake, is the eye-opener. The plans based on that exercise have the best chance to produce a feasible plan towards a clean up.

• The third strategy is to keep on pushing in a bottom up approach among all Government and non-Government stakeholders.

Our role as IHPI is to facilitate the process of support with all our efforts. Further we will work in our role as a network and in the near future extend our own ‘Living Network’ for information and technology exchange, and for training in the Region.

International cooperation on projects here starting at the Forum

The Forum is a facilitating platform, which you all should use to enlarge your own network, and I propose that you turn to Prof Holoubek and Prof Atanassov this evening during and after the Reception and try to make plan how we can cooperate on pesticides issues on project to project basis The IHPI has in its network of Ambassadors committed scientist and advisors who will give a helping hand, when project ideas shall be formed into financial proposals.
And now to the HCH question:
People keep asking me, why we still carry the name International HCH and Pesticides Association, why are the HCH's still taken along?

The reason is obvious – at least to me. Former production of Lindane has caused millions of tons of HCH residuals, which are still in our environment and causing unnecessary dangers for people and our food safety. IHPA has this year made a report “The Legacy of Lindane HCH Isomer Production”, which is now available on the IHPA website. Not with the objective to accuse anybody, but to create the necessary awareness and signal to the Stockholm Convention to take Lindane/HCH in as a new POP.

In this context, I would like to call for an international joint action of industry, technology inventors and suppliers to look for “cheap” technical solutions to tackle the largest inheritance of pesticides production.

The Georgian Exhibition on obsolete pesticides

When I was a couple of months ago in Georgia for the FAO, I was deeply impressed on the way the team for the NIP of the Ministry of Environment, lead by Mr. Givi Kalandadze, which has been able to catalyze all regional inspectors in the country to search OPs Numerous awareness workshops have lead to a nation-wide programme. Even a special awareness officer has been employed who is also here in Sofia. They told me about their plan of an OP exhibition which they organized some weeks ago and was a big success which impressed the political scene in Georgia. Therefore we have asked them to come here and show us their exhibition which could be for many an example on how to create public awareness in your country. I advise each participant to take time for this exhibition which is placed in the room next to the coffee break room.

The organizers of the 7th Int. HCH and Pesticides Forum, 2003 in Kiev

After the enormous changes and difficult working circumstances, we expected we will never see the 7th Forum book, but in a kind of Olympic race Valentyna Pidlisnyuk and her team were able to arrange a beautiful book, which arrived this week in Sofia. Congratulations with that great effort!! Let me show you the difference between 1993 when our first book was published and the new one, so there is progress!

With these words, I welcome you to Sofia and to the 8th International HCH and Pesticides Forum. I myself am looking forward to hearing the presentations and to take part in the discussions with 130 colleagues from 40 countries.

I am convinced we will have some interesting time together, and I am sure new ideas and cross-country cooperation will be born the coming.

Enjoy our Forum.

Prof Dr. mult. Dr. h. c. Konstantin Tertyze

Federal Environmental Agency of Germany

Ladies and Gentlemen, dear Participants of the 8th International HCH and Pesticides Forum!

It is my honour and pleasure to welcome you to Sofia on the 8th international HCH and Pesticides Forum on behalf of the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety and Federal Environmental Agency.

On behalf of participants I want to thank the Foundation “Institute for Sustainable Development” from Sofia and the International HCH and Pesticides Association for their large efforts in organizing the 8th Forum.

It is a great pleasure to see that so many people accepted the invitation to attend this Forum.

The basis of the Forum is the initiative of international group of experts, working on the field of obsolete Pesticides.

The scope of the Forum is to Monitoring of exchange information HCH and obsolete Pesticides.

• Risk assessment
• Investigation strategy
• Remediation decontamination
• Of polluted sites depends on the availability and degradibility of contaminants
• Different agricultural arrangements can increase the degradation of pollutants and accelerate the decontamination of sites
• A Controlled cultivation of specific plants with a high affinity to HCH and other chlorinated pesticides (Phytoremediation)

The Forum is stimulating the attendees in developing solution on “How to deal” with contamination, originated from HCH and other chlorinated pesticides.

These results will be achieved by an active participation of all attendees.

This means that the future cooperation and developments on the initiative and input of the participants.

Ladies und Gentlemen!
Expressing my satisfaction of your coming and participation on the 8th International HCH and Pesticides Forum, I wish you a fruitful discussion an exchange of experiences!
CLOSURE SPEECHES

Dan Joergensen

Member of the European Parliament

I am seriously concerned about the issue of obsolete pesticides in central Eastern Europe, Caucasus and Central Asia. Special attention needs to be drawn to food safety and the economical consequences of exports to e.g. the European Union. The food catastrophe with nitrofen in former Eastern Germany is still fresh in our minds.

Therefore, I fully support the activities of the International HCH and Pesticides Forum to create the necessary awareness, exchange of know how and experiences, creation of regional networking and efforts to acquire the necessary funding to solve these huge and very dangerous problems.

For many years, the issue of obsolete pesticides has been debated but no substantial progress has been made towards actual solutions and the elimination forms our precious environment.

However, the first examples of EU support may be the start of a more systematic approach for the region in the near future. The present EU PHARE project to clean up 1400 tons of obsolete pesticides in Romania, which has been requested by the Romanian government, has shown strong political commitment to eliminate these hazards and could serve as a “demonstration example”. It is possible if governments are committed to solve the issue. Also the Stockholm Convention is the right mechanism for these problems.

I will try to do my utmost to help bringing forward the outcome of the Forum in our parliamentary discussions and those with the European Commissioner for the Environment.

I suggest that the organisers of the Forum should arrange a meeting in Brussels after the 8th Forum in order to find out how we can implement the Sofia results in joint-efforts with the European Commissioner for the Environment.

Finally, I really regret not being able to keep my promise of joining you in Sofia and work together with the Minister of Environment and Waters of Bulgaria, the Head of the Bulgarian Parliament and the Romanian Secretary of State of the Ministry of Agriculture and the Head of the Ukrainian Association of Cities.

Yours sincerely,
Dan Jorgensen
Dear Forum participants,

Let me first apologize for the last minute cancelling of my participation in the planned discussions with the Minister of Environment and Waters of Bulgaria, the Head of the Bulgarian Parliament and the Romanian Secretary of State of the Ministry of Agriculture.

The issue of obsolete pesticides in Central, Eastern Europe, Caucasus and Central Asia is an important problem from the point of environmental dangers, food safety and potential danger to agriculture export, and often confronting the poorer parts of society.

In the European Parliament we have now been dealing more than 5 years with this issue and we still not reached sufficient momentum in order to create the necessary financial support to eliminate numerous of time bombs spread all over the countries in the region.

We have posed many questions on this issue to former EU Commissioner Wallstrom. Even in November 2003, we had fruitful discussions with former Minister of Environment of Ukraine Mr. Ivan Zayets, who made it clear to us how huge the problem in Ukraine with 20.000 to 25 000 tons of obsolete pesticides, spread over 4500 location over the country is.

Yes. We support the objective of the International HCH and Pesticides Forum to create the necessary awareness, and catalyse the necessary funding to solve these huge and very dangerous problems.

We advice to follow the way of direct requests for help to EU Commission in the respective EU financial mechanisms and honestly believe that the efforts of those countries that had prioritised the problems and have requested help have received that help. Albania requested help and in 2001 obsolete pesticides have been destroyed with EU PHARE funds. At present EU PHARE is helping to clean up 1400 tons of obsolete pesticides in Romania, on request of the Romanian government.

We sincerely believe that EU funding requested by the countries and the use of funding provided by means of the financial mechanism of the Stockholm Convention are the right way for solutions.

EU Parliament with its Committee on Environment, Health and Consumer Policy and the many Delegations to the EU-Accession countries and many of the EECCA Parliamentary Committees will try to support solutions of obsolete pesticides in the near future

I would like to invite the Forum organisers the meet after the 8th Forum to come to Brussels and to see how we jointly can follow-up the Sofia results together with EU Commissioner on Environment to work towards concrete solutions.

Yours truly,
Bart Staes

Stavros Dimas
European Commissioner for Environment

As Commissioner of Environment, I have a genuine interest in the work of the International HCH and Pesticides Forum. I would like to congratulate the organisers for the increasing commitment and technology information exchange that your efforts bring. Your individual and collective contrition adds to more international awareness and search for common solutions for the elimination of obsolete pesticides in New EU Member Countries, Accession Countries, European Neighbours and Russia, Caucasus and Central Asian Republics.

The obligation to eliminate obsolete pesticides is clearly a national one. The issue of obsolete pesticides merits indeed high attention in environmental policies and in the national action plans in countries with obsolete pesticides problems. As far as it concerns Member States of the European Union, obsolete pesticides are waste and they must be disposed off in accordance with the comprehensive EU waste legislation. The European Commission is very committed to safeguarding the correct implementation on the ground. Furthermore the Commission is presently preparing a Thematic Strategy on the sustainable use of pesticides.

The European Union has established financial instruments that are available to manage obsolete pesticides in an environmentally sound manner. Programmes such as PHARE, ISPA, TACIS and others give a number of opportunities for the eligible countries. Although the available financial resources need to be shared between many policy areas, I think that much can be done using these instruments.

Finally, there is a strong will to tackle the environmentally sound management of persistent organic pollutants on a trans-national level. The Stockholm Convention is the main international instrument to address this issue and a majority of the substances included in the Convention are obsolete pesticides. I encourage all countries in the region to ratify the Convention as soon as possible. Most countries have already received a first grant being used for the implementation of their National Implementation Plans. The Commission is very actively involved in the implementation of the Convention and has adopted a specific Regulation for this purpose. I would like to draw your attention to the study that we are currently conducting on the completion of certain outstanding waste aspects of the POPs Regulation. A first draft report will be available on our web-site very soon.

I am very interested in receiving information on the outcome of the Forum in Sofia and I wish you all intensive and successful discussions.
Mugur Crăciun
State Secretary, Ministry of Agriculture, Forests and Rural Development, Romania

Dear Forum participants, dear Hosts of the Forum,

It would have been an honour for me to have the final word at this Forum, which is entirely dedicated to the elimination of obsolete pesticides in Central and Eastern Europe, Caucasus and Central Asia Republics, but urgent unpredictable situations, which cannot be delayed, prevented me to join you.

As you already know, now Romania had and still has Obsolete Pesticides problems, as well, but due thanks to the PHARE Project, we are about disposing them and cleaning the territory.

Through this project, until 31st December 2005, we will dispose about 1,400 tonnes in 133 sites, further on eliminating other approximately 800 tonnes.

Why did obsolete pesticides become such a priority in a country as Romania with so many other problems?

In the last years, Romania has faced frequent cases of food poisoning, accidents, and diseases caused by the inadequate use and storage of the obsolete pesticides. The environment damage in the neighbourhood of the obsolete pesticides stores has also become visible.

Obsolete pesticides occur in many of the Romanian villages and endanger the drinking water and the food safety, and people are not able to protect themselves.

For the moment the situation is even worse, as many of the storehouses are flooded in the Southern part of our country. I was this week in the flooded region and could witness the extent of flooding problems and the dangers for our people, animals and environment.

All these have made the Ministry start the action of eliminating the permanent sources of pollution.

After the identification and inventory of the sites where the obsolete pesticides are stored, carried out by Phyto-sanitary Units, the action to identify financing resources has started, and consequently, intensive discussions were held with the EC Delegation in Romania, with representatives from Brussels, and together, they have made possible the development of this PHARE project, which include both community funds and a national contribution of around 25%.

I understand that the obsolete pesticides problems are more or less the same in your countries.

We invite you to come in Romania. We will share our knowledge and experiences with you and maybe this will help you in moving on with similar clean-up campaigns in your own country.

What is our Romanian future perspective?

We have set the following goal whereby we think we will be successful:

1st priority: complete cleaning of the entire territory of Romania, both within this project, and through this project and budget extension.

Therefore, we request the EC delegation in Bucharest and EU Commission to support us in our efforts to dispose all the pesticides wastes on the territory of Romania.

2nd priority: At the same time, we will elaborate a strategy and based on this strategy, we will establish a governmental policy for the prevention of a new accumulation of obsolete pesticides stocks.

The strategy shall include the following elements:

Education of Farmers:

We propose a countrywide awareness campaign, which will inform the farmers on the dangers of obsolete pesticides. If we not able to educate our farmers and change their attitude, we will of course be confronted with the obsolete pesticides problem again.

3rd priority: In the context of Romania preparation for the European Union integration, we will give responsibility to producers and distributors to avoid re-occurrence of obsolete pesticides. On one hand the necessary laws must include and must be completed with “polluter pays principle”.

The Romanian Government has made strong commitment to achieve these two goals. I am confident that we are able to continue these activities and to carry them out successfully.

Let me thank the Organisers again for the opportunity to speak to you about Romanian achievement in this area.

I am looking forward to welcoming you in Romania, and I apologise again for not being present at the Forum discussions.

Dr. Archalus Tcheknavorian
President of AFIDE

Excellencies, Ladies and Gentlemen,

As chair woman for the final session of the 8th International HCH and Pesticides Forum allow me before adoption of the Sofia Declaration to give you some highlights and information concerning my and AFIDE’s involvement in the Forum and the role of AFIDE in the elimination of obsolete pesticides specially in EECCA region.

It is a need before presenting and discussing the achievements of the 8th Forum, first of all to recognize the excellent work under the leadership of Ms. Valentyina Pidlisnyuk for the 7th International HCH and Pesticides Forum in KIEV in 2003 which created the basis for the successful outcome of the 8th Forum as, reflected in the SOFIA Declaration. Her tremendous effort and hard work under difficult circumstances prevailing in UKRAINE at that time of the ORANGE revolution has to be recognized by this Forum. Therefore on your and my behalf, I would like to thank her vividly. It is also important to recognize Prof. IVAN ATANASSOV, without his effort and contribution the 8th Forum could not have been organized in SOFIA with such a magnificent set up and services. Our thanks go to him and the GOVERNMENT of Bulgaria for hosting this Forum.
Ladies and gentlemen, I believe all of you will agree with me that without Mr. John Vigen the Director of the International HCH and Pesticides Association remarkable and tireless work, his personal devotion and persuasion the FORUM could not have progressed so much, by creating a better understanding on obsolete pesticides and their elimination in order to create a safer place for our next generation. Surely these forums have provided to the participants the opportunities to exchange views, achievements and technological advancement, and bringing together stakeholders, Governments, private sectors and NGOs to reflect and collaborate together in order to eliminate the obsolete pesticides which are so dangerous to the health of the people leaving in those neighbourhood. I would like on your behalf and AFIDE to thank him for his contribution to this human cause.

Now ladies and Gentlemen would like to present to you the AFIDE, the NGO Association which I am representing. AFIDE is an Association of former UN Industry and Development Experts with the vision to assist countries in need by enhancing the Governments and civil society capability to respond to the development and Environmental challenges. I have the honour being the President of that association to inform you that AFIDE in order to be closer to the regions and to respond more efficiently to the needs of the countries, has taken steps to create AFIDE chapters, one for eastern European countries with the headquarters in PRAGUE and the other one for the Caucasus the headquarters in Yerevan, in the hope to be more effective in assisting the two regions which have tremendous problems of obsolete pesticides in addition to there economic advancement, both development issues are connected to each other. Therefore AFIDE would be happy with the experience of experts of UN to support the outcome of the Sofia Forum and the SOFIA Declaration. It is well understood that more international, national and multilateral commitment, and more international understanding and attention is needed in order faster and effectively to eliminate the dangerous obsolete pesticides with its negative impact to the health of people and with great consequences to the Economic development of the countries.

Ladies and gentlemen and dear colleagues, I would like also to recognize the contribution of my prominent colleagues of FAO and UNEP for there valuable contribution which made my task pleasant and facilitated the drafting of the Sofia Declaration which received your endorsement. I would like to thank my colleagues and you all participants for your trust and support for my and AFIDE’s contribution to this great conference. I thank the organizers and all of you. FINALLY, as a chair person of the final session of the 8th International HCH and Pesticides Forum I would like to remind you kindly, PLEASE MAKE THE SOFIA DECLARATION A REALITY.

THANK YOU.

Mr. Roland Wiederkehr

Co-founder World Wildlife Fund
Founder “Green Cross”
Former Member of Swiss Parliament

Dear Forum Participants,

After having followed the discussions for the last two days, I am very impressed with the discussions and contributions heard.

I also hear about pensioned persons from United Nations being so active. Remember that many politicians have been doing a lot more of good work after their retirement than in their whole political career before. Think about Bill Clinton, but even more about Jimmy Carter, who started his own Foundation in Atlanta. With his Foundation he is doing all the good things for humanity he should have done while he was President of the US – but for whatever reasons was not able to do. Do we have to send high politicians to pension as soon as possible to solve the problems in the world?

We are here together with scientists, governmental representatives, communities concerned and politicians, and at the start of the forum I mentioned a third category of participants that should help us: the communicators, to help to make the subject a priority.

But also a fourth kind of helpers is missing: the economist. During this Forum I came to the conclusion, that the organizing ministries in the forestry or agricultural sector have very nice people in its rows, but no funds and no power.

As long as we cannot show what it means economically if there is no action, we will not win.

In my conversations with the Crop Protection industry during the Forum they have accepted to take social responsibility and I am very happy to bring this forward here.

In fact some of the obsolete hazards are told to have been produced by members of that industry, and it is wise that they get their insurances involved to help in the cleanup.

In the West there is growing demand for organic food, and soon western food retailers will try to get organic food produced in Eastern countries. What if that food has a basic level of toxic contamination, established (not only but also) by the Pops, PCBs and Obsolete Pesticides washed into the food chain with every rainfall, not allowing to carry the label “organic food”, and therefore forbidden to be imported into western countries?

The World Health Organization WHO has predicted that from 2050 onwards, every second inhabitant of this planet will die of cancer – the most important reason for this being the chemicals around and in us. So Food Safety will become a topic, and countries which are said that they are not able to produce safe food will be economically out of the game. Dear friends from the Eastern countries: this would mean heavy economic losses.

And that’s where we have to raise the awareness: how much business cannot be done in the future, if the threats are not being cleaned up – I think, that’s the only language governments do understand these days, and you have to adapt: learn the language!

Make chemicals and obsolete pesticides a topic of highest economic priority, and you will solve your problems.
Dear Forum participants,

After getting in touch with the organisers of the International HCH and Pesticides Forum, just a couple of days before their Forum, on 20 May 2005 in Sofia, they convinced me of the importance of this issue and therefore I decided to change my travel arrangements in order to join this till then «unknown» Forum.

When I then arrived in Sofia the Polish representative explained about the situation in my own country and in the first moment I could not believe that Poland had these huge problems inherited from former Soviet times.

During the forum I had extensive discussions with the Delegations from Ukraine and Georgia and discussed how to find a way forward for their countries. And again I was struck by the extent of the problem being present in virtually all countries being related to the former Soviet Union. A large exhibition set up by the Georgian Delegation, with representatives of the Ministry of Environment showed how serious the issue is. Pesticides laying around everywhere as former pesticides stores have been demolished due to the lack of building materials for the poorest. Pesticides free accessible to playing children, grazing cattle and so bringing obsolete pesticides in our food chain. Due to rain and wind pesticides are spreading to neighbouring areas and entering ground and groundwater polluting precious ground water and surface water where the poor people extract their drinking water from simple wells. And the worst is that rural population and their governments often are not aware of these “hidden” dangers.

So I decided to carry out all possible efforts to make my colleagues in the EU Parliament aware of this problem, but also to convince them of the need to act.

Therefore I have initiated in September 2005 the first meeting in the Parliament and invited MEPs (Members of the European Parliament) to discuss the issue and the ways towards solutions. During this meeting it was decided to establish a Working Group of MEPs that then could help to move the issue forward and to define clear and achievable goals.

Just before the publication of this book on 1st of February 2006, the first meeting of the Working Group on Obsolete Pesticides has taken place in Brussels. During this meeting we were happy to find more and more MEPs of the New Member countries, as it may be clear that we have to take the lead if we seriously want to eradicate obsolete pesticides from our countries.

We know that there is still not enough done to protect us against the risk related to obsolete pesticides. Various reports and presentations demonstrated the potential impact of obsolete pesticides and other hazardous chemicals on the environment and on problems of soil and groundwater contamination. WHO has estimated that in 2050 every second human being will die from cancer due to contamination in food, water and the environment. There are thousand of tones of obsolete chemicals placed in the Southern and Eastern European countries, which are located without any protection against wind or precipitations.

This broad and important theme requires more attention and action on the international agenda in order to reduce risks to the global environment and to communities. The economic consequences of not taking action could lead to a loss of opportunities for exports in the agricultural and fisheries sectors and for reduced opportunities for the development of sustainable tourism.

The main objective of our meeting on February 1, 2006 was to create an actively functioning Working Group which would create and enforce new harmonised EU policy on defining, registering and destruction of forbidden obsolete pesticides.

The following actions must be taken by the WG:

1. We need to create a hand book with the best practices (we must compare the state of the art in the world) and all results must be used to give recommendations for environmental sound POPs management procedures. There must be set up a different approach to new EU countries, EU Candidate countries, the neighbouring States from South and East of Europe, as well as ex-Soviet Union Republics (here we will be thankful for analysis from MEPs who are members of certain EU delegations and from NGOs.)

2. We should establish Guidelines and supporting measures to make inventory of pesticides and to control their destruction. There are technologies, but are they optimal and fully effective? There must be new facilities established which would support the control of pesticides on their life-chain: from the producers till the end-users.

3. We have to develop and implement education and awareness raising tools. Series of events should be planned to support the environmental issues and to explain the danger of obsolete pesticides.

The outcome of the meeting brought the following action plan:

1. Talks with MEPs who are the coordinators of AGRI and ENVI Committees to bring the issue into their agendas
2. Bringing the issue to the agenda of AGRI or ENVI Committee with the purpose of making a resolution in the committee for the creation of the budget line.
3. Exchange of opinions and closer cooperation among Rapporteur, Shadow and EP advisors
4. Organisation of a special photo-exhibition in the European Parliament by one of the MEPs.

The talks with the MEPs and the EU Commission’s officials should follow in next weeks. I am also waiting for the outcome of the European Meeting of the members of the Crop Protection Association which is scheduled for mid-March.

I hope that till our next meeting some important steps will be accomplished.

Yours,
Wieslaw Kuc
DECLARATION OF THE 8th INTERNATIONAL HCH AND PESTICIDES FORUM

SOFIA, MAY 26–28, 2005

PREAMBLE

The International HCH and Pesticides Forum represents a platform for discussion between stakeholders of all kinds, working on implementation of projects related to POPs, obsolete pesticides and hazardous chemical waste. It acts as a catalyst in the exchange of information on topics essential for the implementation of the Stockholm Convention and other related multilateral environmental agreements, and the environmentally sound management of pesticides, pesticide waste and other chemicals.

The Forum brings together governments, donors, UN agencies, IGOs, NGOs and the private sector for an exchange of information in an open and informal atmosphere.

On May 26 – 28th, the 8th Forum on HCH and Obsolete Pesticides was held in Sofia. This Forum was initiated and enabled by the International HCH and Pesticides Association (IHPA) and hosted by:

– The International HCH & Pesticides Association (IHPA), The Netherlands
– The Ministry of Environment and Waters of Bulgaria
– The National Center for Agricultural Science, Sofia, Bulgaria
– The Institute for sustainable development, Sofia, Bulgaria

At the 8th International HCH and Pesticides Forum in Sofia, 140 participants from 44 countries attended. The Forum was sponsored by several organisations, as detailed below.

Since the last Forum in Kiev in 2003, many countries have become Parties to the Stockholm Convention and are working on the preparation or finalisation of National Implementation Plans (NIPs). Status reports were presented from many Central and Eastern European Countries. The discussion emphasized the importance of good quality NIPs as a basis for implementing sound chemicals and waste management required under these international agreements.

Country presentations demonstrated the potential for the impact of obsolete pesticides and other hazardous chemicals on the environment and for causing problems of soil and groundwater contamination. WHO has estimated that in 2050 every second human being will die from cancer due to contamination in food, water and the environment.

This broad and important theme requires more attention and action on the international agenda in order to reduce risks to the global environment and to communities. The economic consequences of not taking action could lead to a loss of opportunities for exports in the agricultural and fisheries sectors and for reduced opportunities for the development of sustainable tourism.

DECLARATION

The participants of the 8th International HCH and Pesticides Forum representing governments, IGOs, the private sector, civil society and academia, meeting in Sofia expressed their thanks and gratitude to the Government of Bulgaria for its hospitality and generous contribution in organising this Forum.

Furthermore the participants expressed their appreciation for the efforts of the Director of the IHPA and for his permanent support and contribution in keeping the issue of obsolete pesticides on the international agenda.

The participants,

Stress the continuing negative impact of POPs, obsolete pesticides and other hazardous chemicals on human health, the environment, wildlife and natural resources such as soil and groundwater and are aware of the economic consequences thereof,

Recognise the need for ensuring the dissemination of information and public participation in the decision making process regarding POPs, obsolete pesticides and hazardous chemicals,

Recognise the value of high quality NIPs and other studies as foundations for taking action towards the elimination of risks from POPs, obsolete pesticides and hazardous chemicals,

Call for accelerated action on the elimination of POPs, obsolete pesticides and hazardous chemical wastes,

Call upon governments and national organisations of the region to give priority to actions for eliminating POPs, obsolete pesticides and hazardous chemical wastes,

Further call on the EU and other donors to support national initiatives for the implementation of elimination strategies for POPs, obsolete pesticides and hazardous chemical wastes,
Recognise the importance of sound national policies, legislation and chemical and waste management in preventing future accumulations of obsolete pesticides and other hazardous chemicals,

Recommend, after the preparation of NIPs, focusing attention on the identification and formulation of destruction and remediation projects,

Repeat the call, made at the 7th International HCH and Pesticides Forum for the creation of a regional network for the provision of expertise and experience sharing amongst governments, IGOs, NGOs and other stakeholders,

Recognise that effective hazardous waste management is an important component in the prevention of future accumulations of obsolete pesticides and other hazardous chemical waste,

Recognise the important benefits to be gained by the countries in the region from the integration of action under the multilateral chemical agreement⁴,

Acknowledge the role of the EU and the UN system as well as bilateral initiatives (twinning) in the implementation of actions to eliminate POPs, obsolete pesticides and hazardous chemical wastes in the countries of the region,

Call on the wider chemical industry to participate with relevant policies in support of projects,

Welcome and support the initiative for establishing a Central and Eastern European Regional POPs Centre under the auspices of the Masaryk University, Czech Republic and the ICS, Trieste Centre of UNIDO,

Recognise the impact on policy-makers and donors of visual demonstrations of the threats from POPs, obsolete pesticides and hazardous chemicals and the negative impacts of these wastes on human health and the environment. In this connection, the photos of the Georgian obsolete pesticide sites were highly appreciated, and it is recommended that stakeholders organise such expositions in different countries and during conferences as well as in the European Parliament.

STATEMENTS:
The Bulgarian Ministry of Environment

The Bulgarian Parliament

The Romanian Ministry of Agriculture, Forests and Rural Development

Members of European Parliament

The European Commissioner for Environment

The International HCH and Pesticides Association (IHPA) strongly supports the recommendations of the Sofia Forum, by giving assistance to:
– Inventory methods and instruments
– Training programmes
– Programme management
– Quality assurance
– Documentation
– Technology transfer
– Evaluations
– Public participation
– Assistance in the set-up of country networks of important stakeholders

HISTORY
The first HCH and Pesticides Forum was held in 1992 in Zwolle (The Netherlands). It started with status reports on the perception of the problems related to the presence of obsolete pesticides in different countries. During the next Forums in Magdeburg (1993), Bilbao (1994), Poznan (1996), Bilbao (1998), Poznan (2001) and Kiev (2003) the scope of the Forum was enlarged with exchange of information on common practice, technical solutions, risk assessment, the specific problems in Central European and EECCA countries, training, technology development and funding. Over this more than a decade the number of participants has grown from 40 till 140. The number of institutions present in the Forum has increased accordingly.

The value of the International HCH and Pesticides Forum as a whole is the possibility for the ‘pesticides community’ to debate important issues such as technology transfer, partnership and ‘lessons learned’ from failures and successes. This debate brings better understanding, and presents ideas for those preparing and implementing (National) Implementation Plans for obsolete pesticides, management of chemicals and sustainable agriculture, together aiming at overall sustainable development.

It is to be noted that the European Union stresses that Stockholm Convention National Implementation Plans (NIPs) are an instrument to establish priorities and to determine the necessary means to achieve them. The EU further encourages the Parties of the Convention to seek coherence between NIPs and other existing and future plans to be developed in the area of chemicals management. The EU stresses the importance for Parties to use NIPs as a mechanism for enhancing strategies and strengthening cooperation between Basel, Rotterdam and Stockholm Conventions and urges Parties to integrate sound management of chemicals, including NIPs, in their national strategies for sustainable development, national development plans and other national and sectoral development plans.

The above position has specifically been expressed to the 8th International HCH and Pesticides Forum for which official letters of support have been received. Letters from members of the EU Parliament and the European Commissioner to the Environment are especially worthy of mention.

Until now, attention has been given only on a limited scale to the problems of soil and groundwater contamination as a consequence of former stocks of pesticides, especially regarding the medium and long-term negative effects threatening food production and groundwater quality.

**FORUM SPONSORS**
The International HCH and Pesticides Forum in Sofia was sponsored by:

– Ministry of Environment and Waters of Bulgaria
– BalBok Engineering JSCo, Bulgaria
– European Crop Protection Association (ECPA)
– Federal Ministry of Agriculture, Forestry, Environment and Water Management of Austria (BMLFUW)
– Department for Environment Food and Rural Affairs (Defra), United Kingdom
– Swiss Agency for Development Cooperation, SDC, Switzerland
– Ramboll, Denmark
– Tauw Group, The Netherlands
– Orel-G. Holding Ltd., Bulgaria
GEORGIAN EXHIBITION ON OBSOLETE PESTICIDES: EXPLANATION AND PHOTOS

Otar Kiria

Awareness Rising Consultant for the POPs Project of UNDP

This Exhibition was prepared in framework of the Public Awareness Raising section of the GEF project: Preparation of National Implementation Plan on Persistent Organic Pollutants under Stockholm Convention managed by UNDP in Georgia and the Ministry of Environment Protection & Natural Resources of Georgia. The exhibition materials were collected along with the project working group activities. For the preparation of the professional exposition the project has hired the experts of exhibit-art. The Exhibition lasted 3 days and was attended by the presenters of Government of Georgia, Parliament of Georgia, The Ministry of Environment Protection, Diplomatic Corps, International Organizations & Foundations, NGOs, Artists, Famous faces and Media. The Exhibition was broadcasted and published on four nationwide TV Channels, one international Channel, each of international and nationwide radio stations, a number of newspapers, news agencies and online magazines. Therefore millions of people realized that some of pesticides around them are dangerous and should be avoided.

AIMS AND THE SUBJECT OF THE EXHIBITION

The exhibition was aimed at raising the public awareness to the POPs issues and presenting the work done by the project. The exhibition presented the situation in Georgia concerning POPs issues. Namely:
1. How and where the POPs and obsolete pesticides are dispersed countrywide;
2. How the dangerous they are;
3. Why should the society pay extra attention to obsolete pesticides and POPs.

EXPLANATION

Materials expose the obsolete pesticides dispersed near the villages, towns, vine yards, rivers etc. Each of the expositions has got the explaining annotation in English printed on high quality paper.

On the next page a number of photos are displayed.
ENVIRONMENTALLY SOUND MANAGEMENT, APPROACHES AND CONTROL OF OBSOLETE & POPs PESTICIDES IN BULGARIA

Manuela Georgieva

Deputy Minister of Ministry of Environment and Waste in Bulgaria

Persistent Organic Pollutants (POPs) are serious threat for Human health, Environment and life on Earth. In May 1995 the Governing Council of the United Nations Environment Programme (UNEP) requested in its Decision that an international assessment process should be undertaken of an initial list of 12 Persistent Organic Pollutants (POPs), which are:

- toxic chemical substances,
- persistent for a long time before they break down;
- accumulating in the fatty tissue of most living organisms,
- transferred by air, water and, via migrating biological species, across international borders,
- deposited far from the location of their releasing,
- and very likely to have significant negative human health or environmental impacts close to, or far away from, their source.

Since Persistent organic pollutants (POP) circulate globally, no country acting alone can protect its citizens or environment from risk for present and future generations. Recognizing this, Governments have agreed to negotiate a global treaty on POPs beginning in early 1998. In May 2001 at a Conference of Plenipotentiaries, held in Stockholm, Sweden a Convention was adopted and opened for signature, later called Stockholm Convention for Persistent organic pollutants (POPs). It has been signed by 151 Governments and till now it has been ratified by 97 states and the European Community.

The Republic of Bulgaria signed the Stockholm Convention on 23 May 2001, the National Assembly has ratified it by Law on 30 September 2004 and entered into force on 20 March 2005.

As a party of Stockholm convention Bulgaria has undertaken general commitments to take legal measures to reduce or eliminate releases of Persistent organic pollutants (POPs) from intentional production, namely – bans for intentional production, import and export of POPs had been introduced as well as Prohibitions or Limitations for Trading or Use.

According to Article 7 of the convention, the Republic of Bulgaria must develop National Implementation plan for management of POPs till 2007.

I can note with satisfaction that our country has already started the development of such an Implementation plan as a part of a Global 12 pilot countries project, financed by the Global Environment Facility of the United Nations Environment Programme (UNEP). In the pilot protect from Central and Eastern Europe participate only Bulgaria and Slovenia. For the time being, the Bulgarian subproject is progressing successfully and as per preliminary agreed programme. The National Implementation plan shall be endorsed by National Coordinating Committee, including experts from various Ministries, Research Organizations, Universities and NGOs. And will be published on the WEB page of Ministry of Environment and Water. It is envisaged also a strategy for implementation and Specific Action plans for the individual POPs.

As a part of the project, the group of persistent chloroorganic pesticides that are subject to the Stockholm Convention: aldrin, dieldrin, endrin, mirex, toxaphene, hexachlorobenzene, heptachlor, chlordane and DDT had been inventoried.

The results of the inventory have shown that no POPs pesticides have been produced in the Republic of Bulgaria. The available quantities of obsolete and unusable chloroorganic pesticides are due to their import in the 60-ies of last century. With the first appearance of evidence of their harmful impacts on human health and environment, our country has undertaken legal measures and in the beginning of the 70-ies of last century the import and use of POPs pesticides has been banned. After the ban for POPs use in agriculture had entered into force, actions had been taken for replacing with insecticides registered in Bulgaria as suitable for use in any specific case.

The solving of the problem with sound storage of prohibited and unusable plant protection preparation is one of the general priorities of the Ministry of Environment and Water.

For the purpose of environmental protection and aware of the health concern, I would like to present some of the considerable actions that had been taken by Ministry of Environment and Water:

- In 1998 with Orders of Minister of Environment and Water and Minister of Agriculture and Forestry an Inter-Agency Committee of Experts to manage the “prohibited and obsolete plan protection chemicals” had been created. The Committee had developed a Programme at national level, implementation mechanism and criteria for assessment and allocation of grant financial funds for projects related to save storage of obsolete and unusable pesticides.
All municipalities, which apply with such project, receive necessary funds from the Enterprise for Management of Environmental Protection Activities (EMEPA), promptly and as a grant. As a result of the implementation of this programme, many of warehouses, storing obsolete and unusable pesticides have been repaired and transformed into storages with safeguard provided.

- In August 2000, under the project “Destruction of Risk Pesticides from Bulgaria in the Netherlands” from the regions Sofia, Plovdiv, Shumen and Burgas, approximately 30 tonnes of POPs pesticides such as DDT, aldrin and dieldrin were exported and incinerated in Rotterdam, the Netherlands.

- In the period 2001-2003 a total of 397 warehouses have been emptied and the quantities of obsolete and unusable pesticide stored in them have been re-packed and moved to centralised warehouses, or disposed of in BB cubes. The emptied warehouses have been cleaned up.

- For the period 2001-2003, the number of warehouses for unusable and obsolete pesticides has decreased from 772 in 2001 to 651 in 2003, but the number of centralised warehouses has increased rapidly from 16 to 72. Old storage facilities are gradually repaired and the newly repaired are provided with guards. The share of protected warehouses is constantly increasing, in 2003 being 43%, with 11% higher than the previous year. The condition of the warehouses and of the pesticides stored in them is subject to constant monitoring.

- During 2001-2003 the Ministry of Environment and Water through its regional structures continued the constant monitoring and control of warehouse, storing obsolete pesticides. Annually the Regional Inspectorates for Environment and Water collect and send in Executive Environmental Agency Information Cards for the status of obsolete and unusable pesticides. During the period 2001-2003, lasting positive trends toward restriction of the negative environmental impacts of warehouses have been noted.

- In 2003, all obsolete pesticides stockpiles are stored in 72 centralised and in 579 municipal warehouses, as well as in 957 BB cubes. Due to strict control the stockpiles of obsolete pesticides disposed in centralised warehouses in 2003 is 4656 t and in BB cubes amounted to 3559.

- The funds allocated by the Enterprise for Management of Environmental Protection Activities (EMEPA) and National Plant Protection Service have been increasing constantly during the period 2001-2003 for safe storage of obsolete pesticide, repair of warehouses, cleaning up of premises and sites, collection, re-packing, and moving of chemicals from warehouses in small urban centres to municipal and centralised warehouses, or disposal in BB cubes. In 2003, the Ministry of environment and water respectively the Enterprise for Management of Environmental Protection Activities (EMEPA) has allocated approximately 1 652 000 BGN, and the Ministry of Agriculture and Forestry, respectively National Plant Protection Service – 287 472 BGN. For 2004 the Ministry of environment and water has allocated approx. 2 000 000 BGN.

- The data indicate that now approx. 70% of all obsolete and unusable pesticide is stored in a safe environmentally sound manner.

- The conducted by Ministry of Environment and Water consecutive policy, the construction of centralised municipal warehouses, the responsible storage of the available obsolete pesticide stockpiles, the cleaning up of emptied warehouses, and other related activities are evidence of a comprehended problem and proper governmental policy.

This paper presents the results of the project “Environmental sound management of obsolete pesticides in two regions of Russian Federation Pskov and Vologda”. The project is implemented under the Arctic Council (AC) in co-operation with Arctic Council Action Plan to eliminate Pollution (ACAP) where focus on obsolete pesticide management is given to the Arctic and semi Arctic regions. The project was co-financed by both Russian oblasts and has been implemented in co-operation with the Russian regional authorities. Completion is expected during spring 2006. The consulting company Cowi Consult was awarded the contract on implementation.
OBJECTIVES

The long term objective of the project is to reduce the impact of Obsolete Pesticides (OPs) incl. POP pesticides on human beings and the environment in Russian Federation. The short term objective is prepare inventories and store part of the OPs stocks under safe and environmental sound conditions as demonstration of such practices.

ACTIVITIES

The project assisted the oblasts in:
• preparation of inventories of obsolete pesticide stockpiles
• preparation of action plans for future management and disposal of obsolete pesticide stockpiles
• demonstration of safe and environmentally sound management of obsolete pesticide stockpiles.

INVENTORY RESULTS

For Pskov oblast more than 254 sites have been identified with stock of obsolete pesticides. In Vologda oblast 147 sites were identified. The tables below show the different types of obsolete pesticides, the most common active ingredient and the conditions of packaging when the sites were identified.

<table>
<thead>
<tr>
<th>Type of Obsolete Pesticides</th>
<th>Pskov (tons)</th>
<th>Vologda (tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Known</td>
<td>123</td>
<td>96*</td>
</tr>
<tr>
<td>Unknown</td>
<td>399</td>
<td>107</td>
</tr>
<tr>
<td>Empty packaging</td>
<td>22</td>
<td>10</td>
</tr>
<tr>
<td>Contaminated soil, concrete &amp; wood</td>
<td>29</td>
<td>3.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Active Ingredient</th>
<th>Pskov (tons)</th>
<th>Vologda</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl mercury chloride</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>2.4D</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>TCA sodium</td>
<td>17</td>
<td>25</td>
</tr>
<tr>
<td>Sodium metabisulfite</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>CCC</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>HCB and HCH</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Tri-allate</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Copper sulphate</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>DDT (POP)</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Condition of Packaging</th>
<th>Pskov</th>
<th>Vologda</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good packaging</td>
<td>6 %</td>
<td>3 %</td>
</tr>
<tr>
<td>Minor damage</td>
<td>15 %</td>
<td>22 %</td>
</tr>
<tr>
<td>Serious damage or no packaging</td>
<td>79 %</td>
<td>75 %</td>
</tr>
</tbody>
</table>

FEATURES

• lockable doors,
• sufficient ventilation,
• complete roof,
• concrete floor, and
• door ramps

The picture below shows the new storage facilities in Vologda. The facilities were financed by the oblast. All stocks of obsolete pesticides were collected and re-packed by local trained staff and stored in the facilities under environmental safe conditions.

LESSONS LEARNED

The lessons learned during the project were the following:
• Co-financing in place
• National/regional commitment in place
• Federal/regional regulation in place (Stockholm convention, legislation) (driving force)
• Need of Hazardous Waste Management Plan including decision on destruction of hazardous waste (Oblast/Region/Federal)
• Public awareness and public participation (involved authorities, public, NGO’s)
DEALING WITH OBSOLETE PESTICIDE’S HAZARDS IN ARMENIA

E. Manvelyan, L. Simonyan, E. Anakhasyan

Armenian Women for Health and Healthy Environment NGO, Yerevan, Armenia

ABSTRACT
Pesticide usage in Armenia has been always widespread both in agriculture and in public health for malaria control. In 1972 the usage of DDT was officially banned in Armenia. In 1982 all banned and obsolete pesticides were collected and buried in the special place, in Artashat region, nearby Yerevan. More than 500 tones of pesticides, such as DDT, granozan, hexachlorocyclohexane, pentachlophenol, etc, were buried in this site. More than 60% of the buried pesticides were persistent organochlorine toxic chemicals. In the 90-ties all relevant documentation about the burial was lost, as well as the information about the location of the burial. Since 2001 AWHHE initiated the search and further investigation of obsolete pesticide burial. During two years (2001-2002) AWHHE has carried out the monitoring of the burial. Alarming results were presented to several Ministries that could be interested in this problem. Unfortunately there was no response from anyone. Only by winning a tender procedure, a grant was obtained and AWHHE got an opportunity in 2003 to address the aforementioned problem by bringing it to the focus of policy interest, involving all interested and relevant stakeholders. The wide advocacy campaign and lobbying of policy makers on the issue of obsolete pesticide burial was initiated. By the means of mass media and cooperation with Department of Emergency the Inter-departmental Commission was created. As a result the governmental resolution on ensuring of security of pesticides burial was made on 24.04.04.

INTRODUCTION
The Republic of Armenia is a mountainous, land-locked country located in the southern part of Caucasus region. Armenia was one of the republics of former Soviet Union with highly developed industrial and agricultural sectors. In 1991 after collapse of the political system, in the wake of a nation-wide referendum Armenia gained its independence.

The smallest republic of the USSR, Armenia covers an area of 29,800 sq km. of which only 55.7% represent living settlements, with population of 3.2 million people. 66.6% of the population are classified as urban and 33.4% as rural. Pesticide usage in Armenia has been always widespread both in agriculture and in public health for malaria control. At the end of 80-ies about 400-500 thousand tonnes of pesticides, including organochlorines, were used annually. Especially excessive was the usage of DDT. In 1972 the usage of DDT was officially banned in Armenia. The same time the usage of chlorocholinchloride, hexachlorocyclohexane and keltane has increased in agriculture. Before the collapse of the Soviet Union pesticides were imported into republic under the centralized control of Ministry of agriculture. There was a Committee of Chemical Development in Agriculture, and all relevant institutions and organizations were represented in that Committee. Each year it was adopting a list of pesticides permitted for using in agriculture with instruction of dose, frequency of usage and date of expiration. Pesticides were imported mainly from Russia – about 90 percent; the rest - from India and other countries. Pesticides, received by the central stockpile, had been later distributed among rural storehouses. However it should be mentioned, that some violations in pesticides’ usage were observed at that time also. In particular, out of 600 stockpiles of pesticides about 300 did not correspond to sanitary norms, including transportation, keeping, storing and handling, according to annual reports of the Ministry of Health.

Obsolete pesticides are one of the most important and urgent issues among environmental problems in Armenia. In 1982 pesticide a mopping up campaign was conducted in Armenia. All obsolete pesticides, including DDT remains, were withdrawn. The collected pesticides were buried in a special place, in the Artashat region, nearby Yerevan – capital of Armenia. A clay lock (2-2.5 meters deep) was specially constructed for the purpose and more than 500 tonnes of pesticides were buried including DDT, granozan (a mercury containing pesticide, HCH /hexachlorocyclohexane/, pentachlophenol, etc. More than 60% were persistent organochlorines. The lock was built according to instructions and orders, established in previous years and approved by relevant Ministries and Departments. Up until 1989 soil samples were regularly taken from the site to test for possible contamination of the surrounding region.

In 1991 after the collapse of the Soviet Union Armenia gained its independence. This political transition and the long socio-economic crisis in Armenia changed the situation dramatically. Regular investigation of the soil around the burial place was stopped. Almost all relevant documentation was lost, along with information about the location of the burial site.

In 2001 the NGO Armenian Women for Health and Healthy Environment (AWHHE) undertook efforts to locate the site. It was found and lacked any measures to discourage public entry, such as security guards or barbed wire. AWHHE specialists conducted a preliminary investigation of the soil in the area. Out of 11 samples four contained DDT, DDE, HCH at average concentrations of 4.29 mg/kg, about 40 times the national maximum permissible concentration (MPC) of mg/kg in soil. In two of the samples pesticides residues exceeded the MPC by several hundred fold (23.9 and 54.55 mg/kg).

Deep cracks were found in the soil around the site. The integrity of the burial site is further complicated by its location in a landslide area on the top of the hill and only 800 meters from residential sites. In addition, the system of drains and pipes around the burial site had been demolished and
there is now a real threat that pesticides will leak into ground water and the surrounding environment.

The threat posed by obsolete pesticides is now one of the most important and urgent environmental problems in Armenia. With support from the International HCH and Pesticides Association AWHHE has collaborated with ECOCGLOBE to raise the issue of pesticide burial at the highest political levels in Armenia. As a result this issue was presented during hearings in European Parliament in Brussels in spring 2003.

AWHHE continued monitoring the site during 2003 and 2004. Out of 123 soil samples 75% contained DDT, DDE, DDD, HCCH in levels from 5 to 2000 times exceeding MPC levels. Further investigations around the burial site were supported by UNIDO & UNEP through International POPs Elimination Network (IPEN) & International POPs Elimination Program (IPEP), WECF, USAID and PAN Europe.

AWHHE has conducted extensive information and education campaigns among the rural community in the Ararat oblast. They have also successfully lobbied among policy makers both directly and through the media resulting in the creation of an inter-departmental commission focusing on the problem. This resulted in a governmental resolution on ensuring the security of the buried pesticides on 24 April 2004. A fence has now been installed and drainage is restored.

However, despite the government resolution and the measures already undertaken, the burial site is still not fully secure. AWHHE still detects high concentrations of organochlorines both at the burial site and fifty meter beyond the edge of the site.

The activities of AWHHE and the measures taken by the Armenian government’s Emergency Department have increased security reducing the risk of people and animals entering the site. However, the area is still considered an active landslide zone.

This site is not the only one in Armenia. The full inventory has not been carried out but according to information obtained from the Ministries of Agriculture and Nature Protection there are about 200 tonnes (in addition to the five hundred tonnes in Artashat) of obsolete and expired pesticides in different regions mainly located in previous regional centralized stores. Constructive actions need to be undertaken to ensure safe treatment and disposal of the obsolete pesticides at these sites.

**MATERIALS AND METHODS**

- Investigation of the pesticides burial (research institute of Geology, Academy of Science RA October 2003- April 2004)
- Investigation findings on soil samples, vegetation and water from the burial place site and environment (October 2003- April 2004)
- Information, education, mass media and advocacy campaigns (seminars, meetings, Round Tables, TV and Radio programs, articles in newspapers, press conferences)
- Pre-post comparisons of pesticide usage of population of Ararat oblast (surveys 2003-2004)
- Appeal to the prime minister of Armenia requesting action to solve the problem of toxic pesticide burial in Ararat oblast (February 2004)
- Community mobilization through involvement of children in cultural events (theatre events, video film, exhibition)

**RESULTS**

- The Government of Armenia made a decision on ensuring of pesticides burial safety by April 2004
- Awareness among Ararat region rural community member and governmental officials increased by 40% (May 2004)
- DDT, DDE and DDD in breast milk are the witness about constant contamination of environment in the villages.
- The usage of pesticides decreased by 10.8% in Ararat oblast
- The collaborative Committee of Citizens and elected governance established (February 2004)

The measures had been undertaken by Government within the resolution are temporary. The constructive actions have to be undertaken in terms of safe treatment and disposal of obsolete pesticides site. AWHHE recommends inviting the international experts to make a decision on safe methods of treatment and disposal of obsolete pesticide stockpile. To achieve the goal AWHHE enhances collaboration with policy makers and governmental authorities countrywide. That will allow lobbying for important decisions and will contribute to the development of relevant policies on the issues of environmental protection in general and pesticides burial in particular.

**ACKNOWLEDGMENTS**

AWHHE expresses its gratefulness to the International POPs Elimination Network (IPEN), UNIDO, UNEP, USAID, WECF, PAN, International HCH and Pesticides Association for continuous support to bring the problem of POPs in the focus of decision makers.

Photo: Landslide situation around the burial site in Ararat oblast
MANAGEMENT OF OBsolete Pesticides in THE REPUBLIC OF MOLDOVA

Iurii Malanciuc  
Ministry of Agriculture and Food Industry

S. Stasiev  
Ministry of Ecology and Natural Resources

A. Velea, C. Mogoreanu  
State Ecological Inspectorate

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

According to last 50 years statistical data, during the 1950-1990s more than 560 thousand tones of pesticides were brought in Moldova, including 22,000 tons of organochlorinated compounds. However, according to the data\(^1\) and data\(^2\) from the Ministry of Agriculture and Food Industry, the most prominent were Moldselhozhimia\(^3\) and State Ecological Inspectorate the average amount of POPs pesticides out of the total stock of pesticides is about 28-30%.

The absence in the past of controls on pesticides manufacture, imports, transportation, storage, and use have resulted in the stockpiling of now banned and useless pesticides which constitute an acute environmental problem/hazard. In order to find a solution for the ever-increasing amount of obsolete pesticides accumulated in the country a pesticide dump was built in 1978 on the territory adjacent to Cismichioi village, in the South of Moldova. Over a period of ten years (1978–1988) 3,940 tons of pesticides were buried there, including 654.1 tons of DDT.

By the early 1990s, over 1,000 warehouses for pesticide storage have been built in the collective farms. During 1991-2003 about 60% of these were destroyed or dismantled with only 20% of the remaining ones maintained in a satisfactory condition. Significant amounts of obsolete pesticides are stored in the open. The deteriorated packaging enhances the risk of harmful effect on people’s health and environment, some warehouses being situated close to residential areas.

THE HISTORY OF GOVERNMENTAL DECISIONS ON PESTICIDES ISSUES
Obsolete and banned pesticides stocks continue to pose serious environmental and human health problems in developing countries, including Republic of Moldova. Especially rural areas are affected by the pesticides waste, which is scattered around the destroyed warehouses. Many people are unaware of the dangers and health risks of pesticides. Usually people are destroying pesticides stores in order to remove the construction materials. The reuse of contaminated containers for domestic purposes is another major risk for human health.

Since 1997, three Government decrees have been taken aiming at the collection and centralized storage of obsolete pesticides while seeking solutions for their final elimination. The first decision nr 474 was approved at 21 May 1997. The main goal of this decision was to assure pesticides storage in the centralized store at “Fertilitea S.A” in Calarasi district. The above-mentioned store was used before as a central pesticides store on the national level. Also that decision contains a plan of measures for the collection and centralized storage of obsolete and banned pesticides. The plan sets out the following activities: pesticides inventory, chemical analysis of the pesticides, collection, repackaging and transporting to the centralized storage. It was planned to organize training courses on pesticides management for the private agricultural sector and to establish the international tender for pesticides disposal. Due to lack of financial resources and territorial – administrative reforms, local and central public authority did not succeed to implement the Governmental Decisions nr. 474. The populations from Calarasi district protested against a centralized storage of pesticides from the whole territory of the country. The main reason of the protest was dislocation of the store close to river Bic and railway (less than 100 m); trains had affected the construction of store.

The second decision on the pesticides centralized storage was the Governmental Decision nr.30 form 15 January 2001, which was elaborated based on the National Program on Waste Management (Governmental Decision nr. 606 from 28 June 2000). This decision stipulated the centralized collection of pesticides in 3-4 stores in each district for temporary storage. By the time the Ministry of Agriculture shall contact “LAFARGE” cement plant from Rezina district in order to establish a contract with them for pesticides incineration. Attached action plan contains similar activities related to inventory, repackaging, collection and transportation of pesticides as were mentioned in the Governmental Decisions nr 474 from 21.05.97, which was abrogated by this decision (GD nr.30).

The next one decision nr 1543 on pesticides issues was adopted at 29 November in 2002, which stipulated a new requirement related to the pesticides store, instead of 3-4 stores for centralized storage in each districted was propose one in Păpăuți village, in the Rezina district. The selected store was the best one that could be found on the territory of the country. In the beginning this storage was built for the explosion materials used for the construction materials obtained from mining. The storage met all re-

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\(^{1}\) Report concerning the imported chemical substances in the RSSM during the 1950-1985. Kishinev 1985. RSSM

\(^{2}\) Moldselhozhimia – the state company responsible for import of the chemicals substances used in the agriculture sector. Later after the collapse of USSR this state company was transformed into the Fertilitea S.A. which is responsible for the same actions.
requirements for chemicals depositing, it is located far away from the village at 5 km distance, in the forest. The store is large enough to accommodate the big quantities of pesticides planned for storage. The floor in the storage consists of impermeable concrete to avoid absorption of spillages and allows easy cleaning. Also the storage has a fence and soil protection wall. Unfortunately this decision again could not be implemented, due to the political circumstances. The local public authority had strong aversion to pesticides storage from all the country and made big opposition together with population. Finally requirements related to centralized storage at Popauti store were again abrogated.

The last one decision (Governmental Decisions nr. 1389 from 24 November 2003) introduces some changes in the Governmental Decisions nr. 1543 from 29.11.2002, including a new requirement related centralized storage of pesticides in one store in each district. The duties of the local public authority are to select the store and to assure the implementation of planned activity for pesticides repacking, transporting and storage until final disposal.

**CONDITION OF PESTICIDES STOCKS**

Many obsolete pesticide stockpiles have been held in the same stores for decades. In the past, pesticide stores were constructed away from residential areas, in most cases in the middle of vineyards or gardens. Many stores or mixing and filling stations were located close to water resources, due to the need of access to water.

Storage and handling of pesticides, even when products are in good condition, present significant hazards to those working with pesticides, the public at large and the environment. In case of obsolete pesticide stocks, the hazards are greater, and the control of personal and environmental exposure can be much more difficult. As a result, the risk to health and the environment are greater and, unfortunately, in many cases the damages have been made. As pesticides decompose they form by-products, many of which have toxic properties. Some by-products of decomposition are more toxic than the original poison. In the process of decomposition, pesticides can change their physical state, liquids crystallize to solids or solids liquify. Many pesticides, when decomposition progresses, form gases where the volume is significantly to product deterioration. In many instance products to the pesticides and contribute to wider environmental contamination levels exceeding the maximum allowable concentration (MAC) from five times in the Southern zone to 50 times in the Central zone. A research by the Institute for Experimental Meteorology of the State Committee for Meteorology of the former Soviet Union showed that in 1979-1985 about 60% of soil samples were polluted with DDT exceeding the MAC, in spite of the fact that DDT was prohibited in 1970.

Beginning in 1989, due to reduction in pesticide application, investigations showed an anticipated decrease of pesticides-related pressure both in annual and perennial crops. During 1990-1995, the regional Centers of Preventive Medicine of the MOH have analyzed the contents of 28 pesticides' residuals in 10 agricultural crops and foodstuffs. Pesticide residuals were found in 56.4% of the tomato samples and in 40 % of the grape samples, but they never exceeded the MAC. This downward trend has continued in the last years. The percentage of samples investigated during 1995-2002 showing traces of DDT and HCH has decreased every year and only episodically exceeded the MAC. Traces of heptachlor showed up only once. From the foodstuffs, animal products were found to accumulate most: in 2002, DDT residuals were found in 4.5% of samples and HCH in 1.8% of samples. The contamination level of crops was insignificant.

The condition of obsolete pesticide stockpiles varies from village to village and storage conditions contribute significantly to product deterioration. In many instance products are stored in the open where they are exposed to great temperature fluctuations and other damaging conditions, which accelerate the deterioration of pesticides as well as their containers.

It is difficult to ascertain the ownership of old stockpiles as a result of changes in the status of organization, due to land privatization process. State enterprises that have since been privatized, or organizations no longer exist, do not take responsibility for previously accumulated stockpiles of obsolete pesticides. In such cases stocks have become neglected and even basic storage conditions are not maintained. The absence of secure storage in such situations also frequently leads to vandalism, theft of products to the pesticides and contribute to wider environmental dispersal.

In November 2003, the MOD and SDES started repackaging and transportation of obsolete pesticides in a few districts. At the same time, it has to be stressed that no technical solution for final elimination/disposal of obsolete pesticides has been selected so far on the basis of an economical, financial, technical and environmental analysis.
THE UPDATED INFORMATION ON RESTORED PESTICIDES

According to the information available on April 21, 2005 repackaging had been completed (solids completed in sacks but still awaiting drums) at 21 central storage sites. Storage sites had been located at an additional 13 sites, while 3 sites had not yet been identified. No work had begun on repackaging at these 16 sites due to a lack of drums. Some 1,800 tons of pesticides had been fully or partially repackaged and stored by this date. MAFI estimates that MOD and DES have used 60,727 polypropylene sacks, 14,463 plastic drums and 1,200 metal drums in the repackaging effort so far. They estimate that after the repackaging is completed there will be 94,000 polypropylene sacks, 40,000 plastic drums, 3000 of the 100 liter metal drums, 100 of the 200 liter metal drums and 100 of the 50 liter drums. In total there is expected to be 3000 tons of POPs contaminated pesticides and pesticides contaminated soil and drums for final destruction. If funds are made available in time, the work on repackaging and storing should be completed by the end of 2005. However, there are likely to be further delays so that repackaging may not be completed by the time this GEF project is ready for implementation. By the time repackaging is complete the total cost of repackaging, transportation, and warehousing 3,000 tons of pesticides and pesticide contaminated soil and drums will have reached 9.4 million Lei, or approximately US$ 780,000.

This cost does not contain training cost of the soldiers effectiveness, amortization cost of used equipment and techniques. The public local authorities covered all expenses dealing with meals and living allowances for soldiers. Additionally were spent between 20,000 and 50,000 lei for the storage repairs.

Information on repackaging, transporting and centralized storage process, involving the institution which performed these activities, including their geographical location

<table>
<thead>
<tr>
<th>Nr.</th>
<th>District</th>
<th>Quantities of packaging, kg</th>
<th>Stored places</th>
<th>Involved institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Anenii Noi</td>
<td>19 950</td>
<td>Mayorality Bulboaca</td>
<td>MoD</td>
</tr>
<tr>
<td>2.</td>
<td>Telenesti</td>
<td>305 532</td>
<td>Mayorality Ratus</td>
<td>MoD</td>
</tr>
<tr>
<td>3.</td>
<td>Floresti</td>
<td>128 235</td>
<td>Mayorality Timișoara</td>
<td>MoD</td>
</tr>
<tr>
<td>4.</td>
<td>Mun. Balti*</td>
<td>13 700</td>
<td>Alexandreni</td>
<td>MoD</td>
</tr>
<tr>
<td>5.</td>
<td>Criulen*</td>
<td>44 195</td>
<td>Pascani</td>
<td>SDCPES</td>
</tr>
<tr>
<td>6.</td>
<td>Comrat TAUG</td>
<td>77 200</td>
<td>Fertilitea SA/Comrat</td>
<td>SDCPES</td>
</tr>
<tr>
<td>7.</td>
<td>Cădăr Lunga</td>
<td>68 736</td>
<td>Mayorality Gădări</td>
<td>SDCPES</td>
</tr>
<tr>
<td>8.</td>
<td>Vulcanesti</td>
<td>49 000</td>
<td>Mayorality Cismigiu</td>
<td>SDCPES</td>
</tr>
<tr>
<td>9.</td>
<td>Stefan Voda*</td>
<td>201 547</td>
<td>Mayorality Tudor</td>
<td>MoD</td>
</tr>
<tr>
<td>10.</td>
<td>Singerei</td>
<td>86 240</td>
<td>Mayorality Alexandreni</td>
<td>SDCPES</td>
</tr>
<tr>
<td>11.</td>
<td>Cimislia</td>
<td>149 117</td>
<td>Cimislia</td>
<td>MoD</td>
</tr>
<tr>
<td>12.</td>
<td>Dubăsari*</td>
<td>25 270</td>
<td>Porumbeni</td>
<td>MoD</td>
</tr>
<tr>
<td>13.</td>
<td>Dondușeni</td>
<td>65 130</td>
<td>Plant from Timova</td>
<td>MoD</td>
</tr>
<tr>
<td>14.</td>
<td>Briceni</td>
<td>132 030</td>
<td>Mayorality Grumancană</td>
<td>MoD</td>
</tr>
<tr>
<td>15.</td>
<td>Căsănei*</td>
<td>141 714</td>
<td>Mayorality Gradință</td>
<td>MoD</td>
</tr>
<tr>
<td>16.</td>
<td>Ocnița</td>
<td>21 280</td>
<td>Mayorality Clocușna</td>
<td>MoD</td>
</tr>
<tr>
<td>17.</td>
<td>Rezina*</td>
<td>34 120</td>
<td>Mayorality Păpărășan</td>
<td>MoD</td>
</tr>
<tr>
<td>18.</td>
<td>Nisporeni</td>
<td>54 125</td>
<td>Mayorality Nisporeni</td>
<td>MoD</td>
</tr>
<tr>
<td>19.</td>
<td>Soldanesti</td>
<td>35 400</td>
<td>Mayorality Chipeșca</td>
<td>MoD</td>
</tr>
<tr>
<td>20.</td>
<td>Ungheni</td>
<td>77 915</td>
<td>Storage from military range</td>
<td>MoD</td>
</tr>
<tr>
<td>21.</td>
<td>Mun. Chisinau</td>
<td>55 000</td>
<td>Porumbeni</td>
<td>SDCPES</td>
</tr>
</tbody>
</table>

Total 1 897 036

Districts where all working on repackaging and safely storing of obsolete pesticides will be finished till the end of 2005

<table>
<thead>
<tr>
<th>Nr.</th>
<th>District</th>
<th>Quantities of packaging, kg</th>
<th>Stored places</th>
<th>Involved institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cahul</td>
<td>54 228</td>
<td>Mayorality Cahul/ATP- 5</td>
<td>SDCPES</td>
</tr>
<tr>
<td>2.</td>
<td>Cantemir</td>
<td>8 000</td>
<td>v. Ciobalăcia/SA Ciobalăcia</td>
<td>MoD</td>
</tr>
<tr>
<td>3.</td>
<td>Calarasi</td>
<td>123 586</td>
<td>Mayorality  Oniceni</td>
<td>MoD</td>
</tr>
<tr>
<td>4.</td>
<td>Edinet</td>
<td>2 682</td>
<td>Mayorality</td>
<td>MoD</td>
</tr>
<tr>
<td>5.</td>
<td>Hincești</td>
<td>49 895</td>
<td>Mayorality Carpenieni</td>
<td>MoD</td>
</tr>
<tr>
<td>6.</td>
<td>Orhei</td>
<td>35 100</td>
<td>Mayorality Pelivan</td>
<td>MoD</td>
</tr>
<tr>
<td>7.</td>
<td>Râșcani</td>
<td>23 286</td>
<td>Mayorality Recea</td>
<td>MoD</td>
</tr>
<tr>
<td>8.</td>
<td>Strășeni</td>
<td>32 872</td>
<td>Fertilitea SA/Strășeni</td>
<td>MoD</td>
</tr>
<tr>
<td>10.</td>
<td>Basarabeasca</td>
<td>10 420</td>
<td>v. Sâclau/Ltd “Sadic Agro”</td>
<td>MoD</td>
</tr>
<tr>
<td>11.</td>
<td>Drochia</td>
<td>15 300</td>
<td></td>
<td>MoD</td>
</tr>
<tr>
<td>12.</td>
<td>Ialoveni</td>
<td>75 240</td>
<td></td>
<td>SDCPES</td>
</tr>
<tr>
<td>13.</td>
<td>Glodeni</td>
<td>31 945</td>
<td>c. Singerei/“Vast Protect”</td>
<td>SDCPES</td>
</tr>
<tr>
<td>14.</td>
<td>Falesti</td>
<td>61 144</td>
<td></td>
<td>SDCPES</td>
</tr>
<tr>
<td>15.</td>
<td>Leova</td>
<td>25 310</td>
<td>c. Iargăra</td>
<td>MoD</td>
</tr>
<tr>
<td>16.</td>
<td>Taraclia</td>
<td>109 570</td>
<td></td>
<td>SDCPES</td>
</tr>
</tbody>
</table>

Total 2,491,361 kg (approx 2,500 tonnes)

Estimated Amount of Soil and Old Drums Containing High Concentrations of POPs Contaminated Pesticides from Old Storage Sites = 500 tonnes

Total Estimated Amount of Pesticides and Wastes for Destruction = 3,000 tonnes

MoD – Ministry of Defense;
SDCPES – State Department for Civil Protection and Extreme Situations
Up till now, around 1800 tons of these substances have been repackaged and stored. There are 9 districts (marked with asterisk *) from 37 in which the first step of repackaging has been done and other 12 districts the National Army together with Emergency Situation Department are working in. According to information provided by MOFAI it is planned by till the end of 2005 all works on repackaging and safety storing of obsolete pesticides will be finished. The total amount of pesticides is now estimated to be 2500 tons. These activities will be done partially with the support of Millieukontakt (a Dutch NGO, who initiated a regional project on obsolete pesticides, and who agreed to implement such activities in a one of the 37 Moldovan counties), completion of the repackaging and centralization work in other counties will be done as before by the special chemical unit of the Ministry of Defense and the Emergency Situation Department. Milieukontakt will carry out the work of quantifying, identifying packaging and storage of the pesticides in a one county in accordance with FAO guidelines and UN requirements. The Government of the Republic of Moldova will continue the repackaging, transportation and storing the pesticides using the methodology applied previously which does not meet UN standards due to budget constraints which require the use of containers that are not UN approved and which do not allow the chemicals to be identified and labeled in accordance with UN rules.

### Repackaging of Obsolete Pesticides in Moldova, May 18, 2005

<table>
<thead>
<tr>
<th>Type of drum</th>
<th>Volume (liter)</th>
<th>Weight, including the cap (kg)</th>
<th>height (meter)</th>
<th>diameter (meter)</th>
<th>Number (31 March 2005)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastic</td>
<td>120</td>
<td>4,3</td>
<td>0,8</td>
<td>0,5</td>
<td>14000</td>
</tr>
<tr>
<td>Metal</td>
<td>50</td>
<td>13,0</td>
<td>0,4</td>
<td>0,47</td>
<td>100</td>
</tr>
<tr>
<td>Metal</td>
<td>100</td>
<td>21,0</td>
<td>0,6</td>
<td>0,47</td>
<td>1000</td>
</tr>
<tr>
<td>Metal</td>
<td>200</td>
<td>42,0</td>
<td>1,2</td>
<td>0,47</td>
<td>100</td>
</tr>
</tbody>
</table>

**NOTE 1:** 35 bags and 15 plastic drums (120 liter) are used for repackaging of 1 tone of solid pesticides

**NOTE 2:** 10 metal drums of are used for “repackaging” of 1 tone of liquid pesticides

**NOTE 3:** It was planned to repackage 3000 tones of pesticides, including 2680 tones of solid pesticides and 320 tones of liquid pesticides

Storing POPs contaminated pesticides in inappropriate conditions has lead to the contamination of adjacent lands. A survey made by the State Ecological Inspectorate in 2002 in the Nistru River basin revealed a significant level of soil contamination with organochlorinated pesticides (OCP), including DDT and HCH, around most of the storage facilities that were monitored. The concentrations of OCPs in soil regularly and significantly exceeded the maximum allowable concentration even at 200 m from these facilities. In several cases the contamination of surface waters nearby occurred. As a result of repeated pesticides inventory, the warehouses for POPs pesticides were established. The Table below shows this information.

### NEXT STEPS TO BE DONE IN THE FIELD OF SUSTAINABLE MANAGEMENT OF THE OBSOLETE PESTICIDES IN THE REPUBLIC OF MOLDOVA

At this moment the World Bank project is under implementation in the Republic of Moldova. This project has the objective to elaborate a project proposal to the Global Environmental Facility (GEF) in order to support the Moldova Government in the field of the sustainable management of Persistent Organic Pollutants including obsolete pesticides. One of the project components includes destruction of stockpiles of POPs containing and contaminated obsolete pesticides (approximately 1,150 tons of stockpiled obsolete pesticides out of the total 3,000 tons). Within above mentioned project an Environmental Impact Assessment (EIA) was developed as a precondition of the World Bank. According to the EIA, it was scheduled that this amount of pesticides will be taken out for the destruction from the 12 warehouses which are placed in 10 districts with extremely high risks for the environment and population. The rest of OP is going to be handled by other institutions, who are working in the field of obsolete pesticides such as Ministry of Defense with the support of NATO and other International organizations interested in solving of OP problem in the region.
INTRODUCTION

The Republic of Slovenia (20,273 km², 1,996,433 inhabitants, 781,354 employees) is a Central European country. Its chief characteristic is its forestation (over 50%); a bit less than 40% of the area is intended for agricultural production, which has been decreasing in the last few years. In the lowlands, less than 25% is agricultural land. Agriculture represents approximately 5% of GDP and less than 10% of employees of the Slovenian economy. An average farm comprises approximately 4 hectares and has a low productivity rate. More than 90% of all agricultural facilities are private. Most of the farmers (10% of the employees) are not engaged in agriculture exclusively, but are also involved in other complementary activities. Agriculture is often only intended for production for the landowners’ own needs. Slovenia is a net importer of food and agricultural products. The most important agricultural branch is stockfarming, which represents more than a half of the gross value of total agricultural production.

Slovenia has been a member of the European Union since 1 May 2004, which obliged it to harmonize its legislation with European Union directives.

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

– Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal;
– Aarhus Convention on Access to Information, Public Participation in Decision-making and Access to Justice in Environmental Matters;

These are the 12 warehouses posing the highest risk. They hold about 1150 tons of material.

Telenesti
Briceni
Hincesti
Cimislia
Floresti (2)
Riscani
Straseni
Stefan-Voda (2)
Nisporeni
Soldanesti
– Barcelona Convention for the Protection of the Marine Environment and the Coastal Region of the Mediterranean;
– Stockholm Convention on Persistent Organic Pollutants (POPs);
and the following international protocols:
– Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources (LBS Protocol);
– Protocol to the 1979 Convention on Long-range Transboundary Air Pollution on Persistent Organic Pollutants;
– Protocol on Pollutant Release and Transfer Registers.

Due to the aforementioned conventions and protocols, signed and ratified by the Slovenian Parliament, it was necessary to prepare a range of executive regulations and plans for the implementation of these documents. The last one among these plans was the National Implementation Plan for the Management of Persistent Organic Pollutants for the Stockholm Convention, which was prepared in 2004.

**NATIONAL IMPLEMENTATION PLAN**

The Stockholm Convention of 2001 (Official Gazette of the Republic of Slovenia No. 31/04) indicates the following persistent organic pollutants (POPs): aldrin \( (C_{13}H_{14}Cl_2) \) – 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanaphthalene, chordane \( (C_{15}H_{12}Cl_6) \) – 1,2,4,5,6,7,8,8-octachloro-4,7-methene-3a,4,7,7a-tetrahydroindane, DDT \( (C_{15}H_{12}Cl_4) \) – 1,1’-(2,2,2-trichloroethylidene)bis[4-chlorobenzene], dieldrin \( (C_{19}H_{17}Cl_5O) \) – 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo-exo-1,4,5,8-dimethanaphthalene, endrin \( (C_{19}H_{17}Cl_5O) \) – 3,4,5,6,9,9-hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-2,7:3,6-dimethanaphth[2,3-b]oxirene, heptachlor \( (C_{12}H_{10}Cl_7) \) – 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene, mirex \( (C_{19}H_{18}Cl_9) \) – hexachloropentadiene dimer, hexachlorobenzene \( (HCH) (C_{12}Cl_4) \), polychlorinated biphenyls (PCBs) and dioxins/furans (PCDD/PCDF).

This Convention stimulated the Ministry of Agriculture, Forestry and Food, Ministry of the Environment, Spatial Planning and Energy, and Ministry of Health of the Republic of Slovenia to prepare a harmonized National Implementation Plan of problem-solving associated with POPs in the field of industry, connected to the exchange of PCB compounds and destruction of used and old stocks, as well as agriculture, where phytopharmaceutical agents that contain one or more of the compounds listed in the Convention as an active substance are still present.

The National Implementation Plan anticipates the following activities:
– Operative programme for removing PCBs and polychlorinated terphenils for the period from 2004 until the end of 2006;
– Operative programme for preventing the pollution of the aquatic environment with dangerous chlorinated hydrocarbons from dispersed pollution sources;
– Operative programme with waste oils from the electro-industry from 2004 to the end of 2006;
– Agricultural and environmental programme.

For the implementation of our programmes, certain Acts and executive Regulations have already been in force, such as:
– Environmental Protection Act (Official Gazette of the RS, No. 41/04);
– Waters Act (Official Gazette of the RS, No. 67/02);
– Chemicals Act (Official Gazette of the RS, No. 110/03);
– Veterinary Service Act (Official Gazette of the RS, No. 33/01);
– Health and Hygiene Safety of Foods, and of Materials and Articles Intended to Come into Contact with Foods Act (Official Gazette of the RS, Nos. 52/00 and 42/02);
– Plant Protection Products Act (Official Gazette of the RS, No. 98/04);
– Agriculture Act (Official Gazette of the RS, No. 54/00);
– Plant Health Act (Official Gazette of the RS, Nos. 45/01 and 23/05);
– Occupational Safety Act (Official Gazette of the RS, Nos. 11/03 and 11/01).

**Strategy of handling POPs in Slovenia**

By its adopted legislation in the field of phytopharma-
aceutical agents, chemicals and health protection of people, animals and environment, as well as other fields, the Repub-
lic of Slovenia has adopted the legal order of the European Union. Therefore, according to the Stockholm Convention, pesticides containing POP substances shall not be marketed or used. Despite the fact that their use has been prohibited for a longer period of time, they will still, due to their persist-
tence, be subject to routine monitoring of residues in food-
stuff, as well as in agricultural and other products.

**Marketing and using phytopharmaceutical agents**

The Plant Protection Products Act, which was harmonized with the requirements of the basic European Community Directives (91/41/EEC and 79/117/EEC Directives), lays down which phytopharmaceutical agents were registered in the Republic of Slovenia and, thereby, approved for use. The compliance of an individual agent shall be assessed by authorised inspectors. On the basis of their opinion, the Committee for Phytopharmaceutical Agents decides on the registration agents. Pursuant to the conclusion of the Committee and with the consent of the Ministry of Health, the decision on registration or its refusal shall be issued by the Phytosanitary Ad-
mistration of the Republic of Slovenia. Prior to its market-
ing, each phytopharmaceutical agent should be adequately classified, packed, labelled and accompanied by an information leaflet in accordance with the regulations.

Marketing of phytopharmaceutical agents may be per-
formed by legal or natural persons that have their head of-
ices in one of the EU Member States and are entered in the registry. To enter the registry, they should fulfil the pre-
scribed conditions, which include provisions regarding fa-
cilities, equipment and staff, record-keeping and delivery of the report on marketing phytopharmaceutical agents.

**Prohibition of marketing, and the control and use of phytopharmaceutical agents containing POPs**

The executive regulation, Order Concerning the Prohibition or Restriction of Marketing and/or Use of Plant Protection Products Containing Certain Active Substances (Of-
ficial Gazette of the RS, No. 105/01), which prohibits and restricts the marketing and use of certain active substances, also prohibits the marketing and use of the following per-
sistent chlorinated hydrocarbons: aldrin, dieldrin, DDT, endrin, chlordane, heptachlor and hexachlorobenzene.

Inspection control of the marketing and use of phytopharmaceutical agents within the country is being implemented by the Inspectorate of the Republic of Slovenia for Agriculture, Forestry and Food. Agricultural inspectors control the marketing of phytopharmaceutical agents within the country, registrations, labels, instruction leaflets, and composition and usage of phytopharmaceutical agents. In addition to this, agricultural inspectors also control legal and natural persons who market these agents: entry into the register of stores, fulfillment of conditions regarding staff, record keeping and other activities. Until any established deficiencies are removed, the inspector may prohibit the marketing of phytopharmaceutical agents if the legal or natural person does not fulfill the conditions prescribed.

- Pursuant to the Act and regulations issued according to this Act, the agricultural inspector has the competence to:
  - Prohibit marketing of prohibited phytopharmaceutical agents;
  - Prohibit marketing if the shelf life of the phytopharmaceutical agents has expired;
  - Prohibit marketing of phytopharmaceutical agents if it is not compliant with the decision on registration (e.g., packaging, label, classification, marks, instruction leaflets, physical and chemical composition, etc.);
  - Prohibit the use of phytopharmaceutical agents if they were not registered or the prescribed permission was not issued;
  - Prohibit the use of the prohibited phytopharmaceutical agents;
  - Prohibit the use of phytopharmaceutical agents if not used properly;
  - Take samples of plants, plant products, soil, spraying mixtures and other required samples;
  - Order appropriate measures if he/she has discovered an exceeded baseline value of the residues of phytopharmaceutical agents in or on plants and plant products during their marketing, and in case there are data and the suspicion that these products have already been released onto the market, and immediately notify the Health Inspectorate of the Republic of Slovenia of this;
  - Prohibit the use of devices associated with the use of pesticides containing POP substances if there is no sign of an inspection or if it was not regularly inspected.

Agricultural inspectors also control the appropriate education of the operators of plant protection and record-keeping of use. The proper use of phytopharmaceutical agents is also controlled indirectly by inspecting the conformity of the prescribed borderline values of the residues of phytopharmaceutical agents in agricultural products of the manufacturers.

The control of the fulfillment of special sanitary and technical conditions regarding the facilities where marketing is being implemented and where phytopharmaceutical agents are stored is performed by inspectors competent for chemicals. Prior to entry into the registry of stores, the inspector shall determine the fulfillment of the conditions regarding the facilities or equipment of legal and natural persons who market phytopharmaceutical agents and shall prohibit marketing these agents if the legal or natural person does not fulfill the prescribed conditions regarding the facilities and equipment.

**INSPECTION OF THE OLD STOCKS OF PHYTOPHARMACEUTICAL AGENTS CONTAINING POPs**

With regard to the agricultural regime and intensity of the agricultural economy as well as the purpose of using preparations containing POP substances, it may be concluded that their use in Slovenia was relatively small. The results of the analyses of pesticides residues in the soil also suggest the small consumption of POP substances in Slovenia.

To explain the consumption of pesticides containing POP substances, the following facts are important:

- Slovenia has approximately 50% area of forested land;
- In the past, the production of food was mainly of the extensive type but was not sufficient for the needs of the population; therefore, Slovenia also imported the majority of its food;
- The fragmentation of agricultural areas and use of crop rotation led to a relatively small consumption of pesticides by producers.

The consumption of pesticides containing POP substances in Slovenia began with the appearance of new harmful pests, including the following two: the Colorado beetle, which endangered the production of potatoes, and San Jose scale, which caused the deterioration of fruit trees; Forest pests in Slovenia have not caused significant damage; therefore, POP pesticides have not been used in forestry.

Among the pesticides containing POP substances from the list of the Stockholm Convention, DDT was mainly used for controlling the Colorado beetle (Leptinotarsa decemlineata), pests in orchards (Quadraspidiotus perniciosus) and other pests in storage facilities in Slovenia. The consumption of DDT was the most extensive between 1957 and 1962, when the resistance of the Colorado beetle to DDT was established in the territory of southeastern Slovenia. After 1962, the consumption of DDT was in decline. For controlling the vole (Arvicol a terestris) in fenced orchards, approximately 1,000 litres of endrin were used annually until 1989 in Slovenia. Toxaphene (C₃₀H₃₀Cl₈) – chlorinated camphene was mainly used for controlling mice. Dieldrin and aldrin were mainly used against pests in soil and storage facilities, but less extensively compared to DDT. Products based on chlordane, heptachlor, mirex and hexachlorobutadiene were not used in agriculture in Slovenia. In Yugoslavia, mirex and chlordane were not registered.

Due to their negative characteristics, possible old stocks of phytopharmaceutical preparations containing persistent organic pollutants (POPs) represent a potential danger to the environment and people’s health. With regard to the fact that Slovenia did not have accurate, but only approximate, records and estimates of old phytopharmaceutical preparations, since they were also used in the time when Slovenia was still a part of Yugoslavia, it was necessary to prepare an inquiry on the remaining quantities of these substances. This was done by means of a questionnaire intended for traders who market these substances and a questionnaire intended for agricultural producers.

The list of POP substances in the questionnaire included all preparations registered in the territory of the former
Yugoslavia. The list did not include preparations and individual concentration variations of the preparations, since such list would be too long and impractical.

The results of the questionnaire on record keeping of old phytopharmaceutical agents – pesticides containing POP substances owned by traders of phytopharmaceutical agents

The process of using the questionnaire intended for traders of phytopharmaceutical agents was carried out in March 2004. It was delivered to 239 addresses from the list of the registered traders of phytopharmaceutical agents (current data of the Office for Plant Protection of the Republic of Slovenia), 50.8% (121) questionnaires were returned, of which 109 were correctly filled-in and included in the results.

The result of the questionnaire showed that the existing traders do not have preparations containing substances included in the list of POPs of the Stockholm convention on stock.

The results of the questionnaire on record keeping of old phytopharmaceutical agents – pesticides containing POPs in agricultural holdings

The questionnaire in the survey addressed to farm owners in Slovenia included a list of all phytopharmaceutical agents containing POPs registered in the territory of the former Yugoslavia. In addition to these, the list also included agents containing thiodan or endosulfan (C, H, Cl, O,S) and dicrof (C, H, Cl, O), which have characteristics of persistent organic pollutants but are not included in the list of POPs of the Stockholm Convention. Due to the transparency and effectiveness of the questionnaire, the list of phytopharmaceutical agents did not include individual concentration variations of the preparations.

At the end of April 2004, the survey with a questionnaire and letter was sent to approximately 68,000 agricultural holdings in Slovenia – i.e., to all addresses in the register of beneficiaries of subsidies of agricultural products. With regard to the extent of the people included in the questionnaire, we have estimated that we included 95% of the agricultural holdings, i.e., the most active agricultural holdings.

The collection of questionnaires took place in cooperation with the Agricultural Advisory Service and was coordinated by the Chamber of Agriculture and Forestry of Slovenia. Agricultural advisers were informed of the objective of the survey and they offered help in filling in the questionnaire. The time limit for completing and returning the questionnaire was 15 May 2004.

Of all the questionnaires sent, 26.4%, or 17,926, were returned. Of the returned questionnaires, 3.9% of the respondents reported consumption or stocks of phytopharmaceutical agents from the list of the questionnaire – Table 2. The surveys were not filled in by those who did not use phytopharmaceutical agents from the list of the questionnaire.

1,136.75 litres of fluid and 6,019.6 kilograms of powdered phytopharmaceutical agents containing POPs were recorded. Regardless of the actual quantity of substance reported in this survey, the ratio between individual preparations is realistic. The survey has shown that, of the available preparations, mostly those containing the active substance, DDT, (Pantakan, Pepein and Zlatacid) were used, with endrin and lindane following it. The analysis of data reported in the survey has shown that mostly phytopharmaceutical agents based on DDT (86%) were used in Slovenia, with HCH (10%) and endrin (4%) following them. The consumption of other preparations containing other POPs was lower than 0.1%. Mirex was not used in Slovenia. The distribution of POPs on stock is similar, as shown by the inspection of the phytopharmaceutical agents used containing POPs (DDT – 81%, HCH – 9%, Endrin – 10%), whereby the stocks have a slightly higher percentage of preparations based on endrin, which is reasonable, since this substance was the last to be taken out of circulation.

Since the survey was not anonymous, the producer of the survey, the National Chemicals Bureau of the Republic of Slovenia, has complete data on the owners of the stocks that need to be removed. Due to the possible misunderstanding of the names and, consequently, incorrectly indicated data, these data need to be checked, especially in cases of Pantakan and Pepein.

Within the framework of such limited results included in the survey, a favoured use of Pantakan in all regions was confirmed, with Lindane and Pepein following it. In this analysis (Diagram 4), the Ljubljana region shows a relatively high consumption of phytopharmaceutical agents containing POPs if compared with other regions, especially with regard to the Prekmurje and Maribor regions, which have a high percentage of agricultural areas. Concerning the consumed percentage of Pepein, the Dolenjska region is the most exposed; however, the large quantity is the result of two questionnaires, in which a total of 200 kg of this agent (consumed by 2003) was documented. The result of such analysis would have to be examined by experts with experience in the field of the consumption of phytopharmaceutical agents in Slovenia.

The total stock of phytopharmaceutical agents containing POPs reported in this survey in Slovenia is over 1000 litres and over 6000 kg. Since the survey was not anonymous, the producer of the survey (National Chemicals Bureau) also has complete data on the owners of the stocks that need to be removed. Certainly, these are not actual quantities of phytopharmaceutical agents containing POPs that are in stock in agricultural holdings. The number is much higher. It only represents a relation between individual preparations, and, with regard to the number of the filled-in questionnaires, we concluded that the number is at least 20-times higher.

**CONCLUSION**

On the basis of the documents presented, such as the international obligations of Slovenia (EU membership), signed
and ratified international conventions and protocols, adopted legislation, and on the basis of the prepared “National Implementation Plan for the Management of Persistent Organic Pollutants (POPs) for the Stockholm Convention” ratified by Parliament and the survey with the inventory of pesticides containing POPs of traders and agricultural producers, Slovenia may be able to remove, i.e., destroy, the existing stocks of POPs by 2010.

The legislator is aware that the cost, regardless of the fact that we have relatively small quantities of old and useless phytopharmaceutical agents containing POPs, will still be very high and that this problem will probably not be solved without international financial aid and loans. Despite this, these activities lead towards decreasing the stocks and towards increased inspection activities that prescribe appropriate measures and advise the owners of these agents how to act to eliminate them.

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cially when referring to paper (cotton fabric) sacks, which are practically outworn. The older pesticides (since 1972) have been kept in special underground storages, which are made concrete-type and located far from residential areas. There are 13 such underground sites in Uzbekistan, most of which are filled with pesticides, insecticides, containers for these, industrial wastes, etc, and covered with slabs and soil. Most of the sites are enclosed with mesh and guarded. Total area of facilities is 60 hectares, and according to the latest information they contain 17,718 tons of pesticides.

As a legacy of defoliation of cotton fields practiced in the last century, there are agricultural airfields throughout the country. The airfields occupy 461 hectares in total. The contamination level of such airfields by chlorine-organic and phosphorus-organic pesticides exceeds the maximum acceptable concentrations level several times.

The State Committee for Nature Protection of the Republic of Uzbekistan implements state control and interdepartmental regulation in the area of environmental protection. The State Environmental Monitoring adopted by the Government of the Republic includes a list of priority sources of contamination, and areas around pesticides warehouses, underground sites and agricultural airfields.

Results of the State Environmental Monitoring (soil) tests intended to define the amount of pesticides around the warehouses show presence of persistent organic pollutants (POPs). The concentration of POPs in the environment does not exclude their transmission into the foodstuffs and live organisms. Monitoring data of 2003-2004 show that the worst contamination by chlorine-organic pesticides within a radius of 200 meters around the underground storages is in Namangan areas, where the concentration exceeds the allowable level 17 times. The same parameter in Andizhan areas is 16 times, but there are places where the allowable level is exceeded up to 100 times. In Syrdaria areas the level is exceeded 13 times. Underground storages obviously have a negative impact on the environment. According to area Inspectors (of the State Committee for Nature Protection) it is impossible to approach some mortuaries closer than 1-1.5 km without personal protection means. Built 40 years ago, the mortuaries collapse under the impact of climatic fluctuations. As a result, there is a danger of pesticides penetration to underground waters, discharges of toxins, and formation of inflammation sources.

Agricultural airfields, underground storages and chemical warehouses are still the main sources of environmental pollution in Uzbekistan, and problems of disposal and decontamination of these have not been solved yet.

Scientists and researches from the Institute of Genetics of the Academy of Sciences of the Republic of Uzbekistan are engaged in developing environmentally clean bio-technologies for bio-remediation of contaminated soils. It includes development of new bio-preparations based in active strains of microorganisms – destructors of chlorine-organic pesticides.

The situation with old pesticides is a characteristic feature of many of the Central Asian countries. We believe it’s feasible to undertake joint efforts in solving the problem with old pesticides, through creating regional center activities, which focus on finding the ways to dispose of obsolete or useless pesticides.

**IMPLEMENTING STOCKHOLM CONVENTION NATIONAL PLANS: WAYS FORWARD**

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**ABSTRACT**

This paper examines the basis and nature of Action Plans, strategies and measures required to implement the obligations of the Stockholm Convention. Some actions will be the proper business of government. Other initiatives will require technical assistance and may be suitable for funding as envisaged in the Convention’s financial mechanism. Some of these will need to be taken up by non-government organisations /0 in particular industry and civil society groups. The paper emphasises the need to find cost-effective solutions by linking proposed actions with other national strategies and policies, and with ‘country assistance strategies’ negotiated by each country and its development partners. Of importance will be seeking appropriate and innovative financing arrangements and partnerships to meet the pragmatic goals of the Convention: to address POPs risks through the adoption of practical, feasible, viable and available techniques. The paper examines issues related to the Global Environment Facility – the interim principal entity of the Convention’s financial mechanism, in assisting developing countries and countries with economies in transition to meet their Convention obligations and protect their populations and the environment from the risks posed by POPs.
INTRODUCTION

Article 7 of the Stockholm Convention requires all Parties to prepare National plans describing how the obligations of the Convention will be implemented. National planning has been taken up by developing countries and countries with economies in transition with funding from the GEF, the interim principal entity of the financial mechanism of the Convention, using initial guidelines prepared by the GEF and its implementing agencies.

The planning process comprises three principal ‘technical stages’:

- assessing the Country situation through inventory activities – physical inventories of the various chemicals and assessments of legal & regulatory frameworks for chemicals and POPs management;
- determining priorities for addressing POPs issues of concern in the context of national objectives;
- developing the plans necessary to deal with priorities and so move the country into compliance with the Convention.

These technical stages are preceded by the development of mechanisms for coordinating amongst the various government agencies with responsibilities for parts of the POPs ‘life-cycle’ and with industry and other non-governmental stakeholders. Such participatory approaches are emphasised throughout the National Implementation Plan (NIP) development process. National endorsement of the plan, prior to its transmission to the Conference of the Parties, and its subsequent implementation depend upon the continuing engagement and participation of a wide range of stakeholders and their common and joint ownership of the POPs problems that are identified in the assessment and planning process.

The completion of the NIP is, of course, not the end of the process but merely the end of the beginning. It is intended to be a dynamic document that will be enriched by the addition of new data and information; updated and reviewed as action plans are implemented and take effect or as new chemicals are added to the Convention. It may form the basis of national reviews and reports to meet Convention requirements.

Article 7 of the Convention is not the only one to require Parties to report to the Convention. Article 15 specifically requires Parties to report on the measures taken to implement the provisions of the Convention and on the effectiveness of such measures.

The first Conference of the Parties\(^1\) decided that each Party shall submit its first report by 31 December 2006 and its subsequent reports every four years thereafter\(^2\).

Reporting to meet the provisions of Article 15 may incorporate other reporting provisions, for example:

- a review of the success of its strategies to reduce or eliminate releases from unintentional production\(^3\);
- a report on its progress in eliminating PCBs\(^4\).

Furthermore, Parties using DDT in disease vector control are required to provide, every three years, information on consumption and conditions of use to the Conference of the Parties and the World Health Organization\(^5\). Parties seeking to renew specific exemptions for the continued production or use of chemicals in Annexes A and B will also need to provide review reports to support their applications\(^6\).

These continuing obligations mean that information gathering and reporting systems established during development of the NIP will need to be sustained. They form the basis for the support from the GEF not simply for the development of the NIP but for ‘enabling activities’ that build capacities of local stakeholders and strengthen responsible institutions.

Assessments of the current situation

Preliminary national inventories, which form the basis for priority setting and action planning during the NIP process, are all imperfect models. These models may be explicit – for example, the dioxin/furan toolkit, or implicit – for example the assessments of pesticide stocks or PCB equipment, and based on survey methodologies that likely provide returns from only a portion of the real populations.

The recognition of the inventories as models gives rise to a number of questions for those responsible for implementing the Convention at national level and for the Conference of the Parties:

- How well do the inventories reflect reality?
- How can the inventories be improved and refreshed?
- Can the initial inventories be used as the basis for indicators of the performance of a Party?

How well do the inventories reflect reality? This question leads to the consideration of whether the inventory is adequate for the purposes of setting priorities and making appropriate action plans.

In considering these questions it is perhaps best to distinguish between the size and shape of the inventory result.

The size refers to the number of items of, for example, PCB equipment, the tonnage of pesticides, the grams of dioxins and furans released in total or in the various components of the inventory.

The shape refers to the distribution of the total inventory between its different components; for example, the proportion of transformers held by the electrical utilities and other sectors of the economy; or the economic sectors contributing significantly to the dioxin inventory.

Inventory size and shape are considered in the simple matrix set out in Table 1 below.

If we have chosen an appropriate methodology and applied it diligently, then our results may reflect the national distribution of the chemical or equipment being considered and our inventory falls in the ‘shape right’ column of the table. Clearly, if we have also been able to gather data from all sources then we may obtain the correct size so that inventory falls into the upper ‘size right’ row. In this circumstance, we have an excellent result that truly reflects reality and forms a secure foundation for planning.

If, as we have suggested is more usual, the true size of the inventory is not captured by the preliminary inventory then our inventory must be considered in the lower row of the

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2. UNEP/POPS/COP.1/CRP.14/Rev.1.
3. Stockholm Convention Article 5 paragraph (a), (v).
matrix. If we have chosen an appropriate methodology and applied it diligently, then our results may still fall into the ‘shape right’ column and we have what is probably a typical result, allowing us to identify areas of priority but underestimating the full scale of the problem.

The worst case is where our inventory has captured neither the size nor the distribution of the problem. Such a result, falls into the bottom right ‘size wrong’ – ‘shape wrong’ cell of Table 1. We must seek to avoid this in the NIP development projects, as the result is practically useless for planning purposes; identifying neither the areas of concern nor the scale of the problem.

None of the inventory methodologies includes means of estimating errors so that imperfections in the inventory will need to be identified in our reporting of the results. Here, local knowledge and our understanding of the technical and socio-economic circumstances surrounding POPs use will be important; they form a ‘commentary’ to the inventory – identifying likely areas requiring further work; estimating possible totals from partial results and so on.

How can the inventories be improved and refreshed?

Clearly, there is limited time and money within the enabling activities so that full and detailed inventories are impossible in most countries. It follows that activities to improve the inventories need to be incorporated into plans to implement the Convention. Of course, these subsequent phases of inventory work will not be national in character but will focus on priority areas or sectors. Here again, if our preliminary inventory is in the ‘shape right’ column, then these more detailed inventories will be correctly targeted.

That more detailed and focused inventories are necessary should not be a surprise to planners or financiers of Convention implementation. It would be unrealistic, for example, to expect to develop from the preliminary national inventory the detailed technical specifications necessary for a contract to dispose of PCB equipment. In this example, disposal of PCB equipment in a key sector would begin with focused inventory work using a methodology like that provided under the Basel Convention (www.basel.int). Of course, results from such inventories should be captured by the national authorities responsible for Convention implementation to enrich and improve the information held at national level.

Can the initial inventories be used as the basis for indicators of the performance of a Party? With clear indications that the inventory results do not capture the true size of the problem, and with no clear measure of error in the inventory models, it is difficult to see how the results can be used to define a baseline against which later national reporting can be compared.

Parties to the Convention have committed themselves to eliminating and reducing POPs emissions and releases and so might expect national reporting to show a progressive fall in national inventory levels. In Diagram 1 (below) I have attempted to show the possible evolution of a national inventory by considering the ‘forces’ acting upon it.

The preliminary national inventory, prepared during NIP development, is represented by the shaded box straddling the vertical axis (time = 0). In the period immediately after its preparation, few, if any, reduction efforts have begun but national POPs teams may well continue to acquire new information and to improve their knowledge and understanding of POPs. In this way, at the time of first national reporting, represented by the next shaded square, the inventory total may have increased. This situation may persist for several reporting periods but it is likely that, as time goes on, the volume of new information decreases (marked by progressively smaller dashed arrows) while the reduction efforts begin to take effect (marked by progressively larger solid arrows) so, eventually, bringing the inventory total down.

In some cases, preliminary national inventories may be characterised by a large proportion of unknowns. For example, ‘suspect’ items of PCB equipment that were produced during the phase of PCB production and use but that, on inspection, lack information on the dielectric fluid used. Sampling and analysis of these items may show a significant proportion to be non-PCBs containing and to eliminate them from the inventory.

Improved knowledge and more complete information progressively reduce the error on the total inventory (shown by the narrowing of the area between the upper and lower dashed error limit lines) but this cannot be easily quantified.

**ACTION PLANS, MEASURES AND STRATEGIES**

Having established the country situation, Parties can begin to plan the actions necessary to move towards compliance with the Convention.
Formal Action Planning is required of Parties at only two places in the Convention: in relation to reducing the unintentional production of POPs (Article 5) and in relation to the disease vector control to reduce and eliminate DDT use (Annex B). This latter obligation is limited to those Parties that request an entry in the DDT register to permit the continued use of DDT in disease vector control.

In addition to these two obligations, however, the English text of the Convention contains more than 200 other uses of the word ‘shall’ implying action by somebody. Some of these are duplications and not all require actions by Parties but, even removing these, there are many references in the convention to actions, measures and strategies that need to be planned in the context of NIP development and subsequently implemented.

The Convention is helpful in providing definitions of the likely contents of an action plan (text box) and further assistance is available from the initial guidance prepared by UNEP and the World Bank[7] and by UNITAR[8]. The purpose of the plans is to identify the objectives and activities necessary to address the obligations set out in the Convention; to identify those likely to be responsible for undertaking the action, and those other stakeholders who need to be involved; to identify the resources and timescale needed to execute the activities; and to rank the actions in terms of both Convention obligations and national policies and strategies towards broader development targets.

Several distinct types of action can be identified in the Convention: there are actions relating to the responsibilities and roles of Parties within the Convention, and its management at national level; to the reduction and elimination of POPs production, use and trade through technical actions; and to social requirements in terms of raising awareness and providing information to vulnerable groups. It seems likely, therefore, that these actions will require the involvement of different groups of actors, different levels and sources of funding, and different modes of operation.

Some actions – for example, the development, maintenance and sharing of POPs data and information and national reporting to the Conference of Parties and its subsidiary bodies, will be the proper and normal business of government and will need to be planned into the work of appropriate line ministries.

Other actions, particular those of a technical nature, may be beyond the current capacity or capability of developing and transition economy states and be suitable for support under the Convention’s technical assistance provisions and for funding as envisaged under the Convention’s financial mechanism (Articles 12 and 13 of the Convention). Guidance to the financial mechanism on those areas of Convention likely to require technical assistance is set out in decision SCI-22 of the First Conference of the Parties.

Some of these plans may require actions by non-government organisations - in particular industry and civil society groups, or be best executed by such groups. Civil society groups with strong community links can be instrumental in raising awareness of particular risks and in assisting the vulnerable to play an active role in designing and implementing solutions. Similarly, the precautionary approach adopted by the Convention places a duty on industry to adopt, or work towards the application of available, feasible and practical measures that locally may represent Best Available Techniques (BAT) and Best Environmental Practices (BEP). Many of the possible approaches listed in the guidance on BAT/BEP in the Convention (Annex C Part V) are, if introduced intelligently, likely to provide economic as well as environmental improvements and thus represent positive drivers for the engagement of industry.

It is recognised, however, that government will need to play an active role in moving into compliance with the Convention. It is important to remember here that while the Ministry of Environment or an equivalent agency is responsible for leading NIP development, it is likely that many of the actions identified as necessary for compliance will fall outside its mandate and require coordination and interaction with a wide range of other governmental and non-governmental institutions. Identifying appropriate stakeholders, defining their roles and responsibilities, and working with them to identify appropriate and workable actions are thus key elements of the planning aspects of the NIP work.

Here again the Precautionary Approach is fundamental. Costs likely to be incurred in the remediation of POPs contaminated sites, if possible at all, are likely to be orders of magnitude greater than the costs of environmentally sound management. For this reason, we need to be sensitive to the risk that our actions to ensure good management of POPs if not properly targeted or designed may result in chemicals, equipment and articles being dumped or moving from the legal sector - where environmentally sound management can be developed, to the informal or illegal sectors where our influence is likely to be much less.

**DETERMINING THE COST OF COMPLIANCE**

Governments becoming Parties to the Convention will be concerned about the costs associated with moving into compliance, and about who will bear the responsibility for providing the financial resources to meet these costs. Governments will expect those developing NIPs to examine a wide variety of alternative actions in order to determine the most
cost-effective approach, and to develop or initiate a resource mobilisation strategy.

Priority setting and action planning during NIP development thus play a key role in examining alternatives and establishing the most acceptable and cost-effective combination of actions to deliver the desired outcomes. Planning is likely to be dependent not only on technical and scientific priorities but also on prevailing socio-economic factors at national level, the results will be a compromise between them.

It follows that action planning is not straightforward but a complex and iterative process. It is likely to involve problem analysis, so that correct interventions can be identified, stakeholder analysis, so that appropriate actors can be identified, and comparative ‘cost-benefit’ analyses of both the status quo and possible alternative strategies.

That POPs possess toxic properties, resist degradation, bioaccumulate and are transported across international boundaries; makes such cost-benefit analysis particularly difficult at the national level. Restrictions in use or the elimination of releases in one country may appear to generate only costs at the national level while benefits accrue elsewhere.

This could jeopardise action were it not for the Convention’s emphasis on identifying cost-effective solutions targeting sources of POPs release, and its intention to offset incremental costs with financial support.

Furthermore, the Convention is helpful in providing a variety of mechanisms that work to reduce costs and provide resources:

- It is founded on precautionary approaches that seek to remove the threats posed by POPs chemicals at source; before they enter the environment or affect human health;
- It provides a variety of timescales during which the chemicals, equipment or articles must be reduced or eliminated. This allows, for example, well managed PCB equipment to be replaced over 20 years, largely according to the normal business capital investment cycle, thus reducing the incremental cost by discouraging the replacement of equipment with residual value;
- It requires Parties to establish and set national targets for the ‘continuous and meaningful reductions’ in the unintentional production of POPs through the introduction and promotion of practical, viable, and available techniques;
- It recommends cleaner production approaches that may provide economic benefits, again reducing or eliminating medium- and long-term incremental costs;
- It stresses the importance of using techniques that are already commercially proven in order to avoid the costs associated with the development and proving of new technology;
- It encourages the linking of POPs obligations to wider development strategies so that costs can be shared and benefits enhanced;
- It defines the obligation of developed country Parties to assist in providing new and additional resources;
- It limits the obligations of developing country Parties and Parties with economies in transition to implement measures to the extent that financial resources, technical assistance and technology transfer are made available; and finally,
- It provides a mechanism for the provision of financial resources and establishes the Global Environment Facility, on an interim basis, as the principal entity entrusted to operate the financial mechanism.

Of course, determining the costs associated with action plans is not easy. The inventory process, as we have seen, provides only a model or outline of the country situation and this will not be sufficient for commercial service providers to calculate or offer firm prices for management and disposal work, or to determine an appropriate timescale for its execution. It follows that action plans of this type will need to be focused on priority issues and incorporate a component of detailed survey and inventory work so that the technical specifications of required work can be determined as a basis for costing.

Furthermore, while prices may be available for key stages of a process – for example, the ‘ex works’ cost of destruction; prices for other stages may be highly dependent on a wide variety of factors. This is likely to make cost estimation in any detail extremely difficult unless similar local experience is available.

For example, costing a plan to remove obsolete pesticides will require a detailed assessment of: the materials to be disposed; the degree to which they require handling and repacking; the degree to which hazards are increased by the decay of packaging and the mixing of stored materials; the access to and security of existing locations and storage facilities; the availability of properly-equipped local service providers; the distances over which materials must be transported and hazards on the way; and so on. Despite this, results from the increasing number of bilaterally-funded removal projects may provide evidence for preliminary costs to be estimated.

In preparing NIPs, country teams may choose to provide more detail and better cost estimates for short-term, priority actions – perhaps based on the results from previous similar exercises, while the costs associated with medium- and long-term actions are left less well defined.

FINANCING ACTION PLANS

Developing country Parties and Parties with economies in transition are provided with a financial mechanism to help them meet the agreed full incremental costs of implementing measures to fulfil their obligations under the Convention. Incremental costs are those additional capital and recurrent costs incurred by the requirement to amend existing practices and act in accordance with the Convention.

Furthermore, the Convention indicates that the source of much of this financial support should be, but is not necessarily limited to, developed country Parties and that it is to be provided either through the financial entity, the GEF, or through bilateral, regional and multilateral sources and channels.

It follows that the development partner community – bilateral donors, regional development mechanisms, the GEF Agen-
cies and needs to be engaged in the process as it progresses. Of prime importance here is for national action planning to be closely linked to and integrated with wider policies and initiatives related to national development – for example, strategies towards the Million Development Goals. This demonstrates Government’s understanding of the purpose and benefits of the Convention and commitment to its role as a Party. In turn, this facilitates the incorporation of POPs targets and priorities in assistance strategies negotiated periodically between Government and its assistance partners. Without suitable references of this type, it is likely to be more difficult to secure bilateral financial support.

Similarly, contributions from the regular government budget to support those necessary and continuing actions required of Parties – the maintenance of a national focal point, national reporting and information provision and exchange, public awareness and education and so on, further demonstrate government commitment and encourage external support.

Nevertheless, country teams will need to minimise the burden placed on hard-pressed local budgets. This can be achieved by:

- exploiting the management synergies between the various chemicals and waste-related multilateral environmental agreements will be important, particularly in small environment departments where de facto only a small number of people are available to handle these international commitments and their national repercussions;
- linking proposed actions with programmes and activities in other ministries and department to derive co-benefits and cost-sharing.

It follows from this that no single financing model is adequate to describe the arrangements that are likely to be necessary to fund implementation actions and NIP development teams will need to be aware of funding opportunities, to develop partnerships and consortia to take initiatives forward, and to seek innovative arrangements of securing national and international, public and private resources.

**THE GLOBAL ENVIRONMENT FACILITY (GEF)**

Established, on an interim basis, as the principal entity of the financial mechanism of the Convention, the GEF is likely to be a significant and critical source of funding for POPs actions in developing country Parties and Parties with economies in transition. The GEF has responded quickly to the Convention, establishing a new focal areas for POPs and providing support to more than 120 countries engaged in enabling activities leading to NIP development and to a range of other demonstration and strategic research initiatives. The provisional guidelines, criteria and priorities set for its operation programme on POPs (OP14) have now been supplemented by guidance provided by the first Conference of the Parties.

The GEF has a number of key advantages that enable it to play this key role:

- It made available a significant of money (US$ 250 million) for POPs over the years of the 3rd phase of the GEF to 2006 and is planning similar or enhanced budgets for the 4th phase to 2010;
- It has the potential and resources to support major & costly environmental projects beyond other scope of most other individual grant donors;
- It routinely makes available grants for project development (PDF-A, PDF-B);
- It is intended to be a transparent and country-driven process; its global agenda is driven by guidance form the Convention and has set objectives and priorities that are publicly available in its programme documents.

There are, however, a number of issues that country teams need to be aware of in considering the GEF as a funding partner for their priority actions:

- It has a lengthy project cycle with full-size projects, where the GEF contribution is expected to be in excess of US$ 1 Million, taking perhaps 2–4 year from the first expression of a concept to its implementation;
- Incremental cost calculations for POPs are as yet unclear and potentially complex and the GEF funds, in principle, only that element of the incremental cost relating to global benefits and requires other funding partners to meet the incremental costs associated with local benefits;
- Only enabling activities are fully funded; all other project types require cofinancing at least equivalent to the GEF contribution so that country teams must explore funding possibilities from other donors, many of whom are themselves contributors to the GEF;
- It places emphasis on projects exploiting new and innovative approaches rather than on projects that represent ‘routine’ or repeated implementation actions at national level;
- It faces competing programmatic pressures that may make it difficult to coordinate GEF and Convention priorities both within and across its focal areas;
- It is introducing allocation arrangements, based on country performance and potential to generate global benefits, that may adversely impact on least developed country Parties and Parties that are small island states that have particular requirements and special needs in terms of capacity and capability development and technical approaches, and are a focus of attention for the Convention.

While these may appear significant obstacles to implementing the Convention, the GEF Agencies have considerable experience of assisting national teams to develop and submit proposals to the GEF. A number of implementation projects have been successfully promoted to the GEF and its partners and this process is likely to accelerate as country teams complete their NIPs and transmit them to the Conference of the Parties.

It follows that country teams developing NIPs should seek the advice and support that is available from the GEF agencies during action planning so that subsequent proposals can be properly founded on priorities and actions highlighted in the NIP.

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10 UNEP/POPS/COP.1/31 decision SC-1/15 Technical assistance.

12 Smaller projects have reduced project cycles and can be implemented more quickly.
CONCLUSIONS: PROMOTING GOOD ACTION-BASED PROJECTS TO THE GEF

The NIP represents the culmination of a lengthy planning process and is the foundation for the implementation of action to reduce or eliminate POPs releases. The preliminary inventories are unlikely, this first time, to reflect the size of the problem in a country but can, with a good methodology diligently applied, determine its distribution or shape. Where the distribution is known, the priorities and action planning can proceed with some confidence.

The Convention is based on the precautionary approach and seeks to engage practical, available and feasible measures to address POPs threats. It is pragmatic and practical in character and realistic, 'concrete' actions need to follow from the planning phase.

The actions necessary to address POPs problems are likely to require the engagement of a wide variety of stakeholders from different sectors of the economy and operating at different levels of society. Government, industry and civil society groups all have important functions in Convention implementation. Similarly, responsibility for POPs actions is likely to extend beyond the mandate of the focal ministry and will require carefully coordination and collaboration between line ministries and other institutions.

It is important that such collaboration and commitment is obtained during the NIP development phase and constituted in such a way that it can continue after the completion of the NIP. This continuing responsibility, likely to form part of 'normal government business', is required to coordinate the diversity of POPs actions and to provide the materials for the Parties continuing reporting commitments to its Conference of the Parties.

Many of the actions identified as priorities in the NIP will be suitable for technical assistance support. The GEF is likely to be a significant and critical source of funding but is never the only source of finance for such operations. Co-financing at least equivalent to the GEF funding is required and country teams will need to be conversant with the programmes and priorities of potential donor agencies in order to build successful funding consortia. Project teams also need to be aware of the complex project cycle of the GEF, particularly where Full Size projects are proposed.

Even with such support, the likely total global cost of implementing the Convention means that Projects designed to introduce environmentally sound management and disposal will need to demonstrate measurable impacts and cost-effectiveness, perhaps through the calculation of 'unit abatement' cost. Parties will need to undertake careful problem and stakeholder analysis to determine the best interventions to remove sources of releases. Similarly, there is a clear need to link POPs actions to other national and regional initiatives to derive the significant co-benefits available.

The many stages in the management and disposal of POPs chemicals, and the problems of determining incremental costs, mean that preparing project budgets can be difficult. Nevertheless, the growing body of information from such projects can provide indicative costs for planning purposes.

While the GEF expects proposals to be country driven, a number of agencies are now available and ready to assist country teams to translate the priorities actions identified in their NIPs into proposals worthy of support.

ACKNOWLEDGEMENTS

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менение на высокотоксичных продуктов для за-
щиты растений нанесли почти необратимых из-
менений в равновесии агроценозов.
В обстановке таких сложившихся обстоя-
тельств пришлось приступить к переоценке из-
пользуемых технологий в защите растений. Экс-
pertная комиссия правительства стала запреще-
ние для применения на ряд пестицидов - гекс-
<норцл<енхс<ан (ГХЦГ), ртутные соединения,
метил-паратрон, паратрон и другие. Установи-
лся новый экологический подход в борьбе с болез-
нями и вредителями сельскохозяйственных куль-
tур и таким образом было положено начало вве-
дению интегрированных систем защиты культурных растений. Конечная цель была ограничить применение средств защиты растений и употреблять их разумно, только при доказанной необхо-
dимости. Разработаны “Пороги экономической вредности” для вредителей и болезней. Разреше-
но осталось зарегистрировать на тех средства за-
щиты растений, которые разлагаются быстро и не загрязняют окружающую среду, менее ток-
сичны для человека и животных.
В семидесятых и восьмидесятых годах прошло-
го столетия, в результате запрещения использо-
vания сильно токсичных пестицидов и в резуль-
tате централизованного планирования и распре-
dеления пестицидов, в стране накопилось более 2500 тонн запрещенных для дальнейшего исполь-
zования, залежавшихся и пришедших в непригод-
ность средств защиты растений.
Накопление непригодных и запрещенных к при-
менению пестицидов является проблемой во мно-
gих стран мира [1-4]. В соответствии с Базель-
ской Конventionей классификации веществ как “опасные отходы” [5]. Ответственными инсти-
tуциями по этой проблемой в Республике Бол-
гария являются Министерство земледелия и ле-
сов, Министерство окружающей среды и вод и их подразделения.
С наступлением времени после 1989 года и рас-
формированием существующих агропромыш-
ленных комплексов, часть из складов осталась без реальных собственников, а это создало реальную угрозу загрязнения компонентов окружающей среды — воды, воздуха и почвы. Имея виду эту проблему общественного значения, в 1991 году Ми-
нистерство земледелия и лесов Болгарии органи-
зовало инвентаризацию складов для сохранения пестицидов. При этом были насчитаны 1500 тонн продуктов защиты растений с истекшим сро-
ком годности. Из этих количеств были отобраны образцы и был сделан химический анализ для ус-
тановления пригодности и при отсутствии серьезных отклонений в составе и свойствах, были использованы по первоначальному назначению, а часть из запрещенных пестицидов была экспорти-
рована в страны, где разрешено их применение.
В 1996 году была разработана программа, кото-
рой включала два этапа и механизм для ее прило-
жения по годам. Основная цель программы была предотвратить нежелательные инциденты и осущес-
твление постоянного контроля запрещенных и непри-
годных к употреблению пестицидов.
Первы этап программы включает организацию сбора непригодных пестицидов в базовые склады по областям. В эти базовые склады были собраны в основном запрещенные к употреблению пести-
циды, содержащие: ГХЦГ, ртутные соединения,
метил-паратрон, паратрон, монокротофос, ди-
нитроортокрезол (ДНКО), каптафол и др.
При инвентаризации складов непригодных пес-
тицидов, которая проводилась в конце 1997 года,
комиссия установила, что в результате избыточ-
ного снабжения, запрещения и ограничения упот-
ребления средств защиты растений накопилось около 4391 тонн пестицидов, собранных в 1268 складах хранения. Из этих складов: на 31 застро-
или окна и двери и таким образом к ним был прек-
рашен доступ, в 23 были собраны пестициды, под-
лежащие уничтожению. Усилили охрану 676 из ска-
дов хранения, что составляло 53% из их об-
щей численности. Существенной оказалась проб-
лема собственности складов — 85 из них оказались без реальных владельцев, а 159 перешли во вла-
дение местных управленческих и сель, после при-
остановления деятельности ликвидационных со-
бсов.
В 1998 году была создана Межведомственная экспертная комиссия на основании совместного закона Министра земледелия и лесов и Минист-
ра окружающей среды и вод. В составе этой ко-
миссии были включены эксперты Министерства окружающей среды и вод, Министерства земле-
делия и лесов, Национальной службы защиты ра-
стений, Государственной агентии “Гражданской за-
щиты”, Министерства труда и социальной поли-
тики, Министерства финансов. Разработано было и Положение о деятельности Межведомстве-
ной экспертной комиссии.
Основными задачами этой комиссии являются:
• Подкреплять Министра окружающей среды и вод и Министра земледелия и лесов в органи-
зации и осуществлении деятельности в связи с работой по сбору, перезатарированию, погрузочно-
разгрузочных работах, транспортированию, охра-
не и обезвреживанию запрещенных, устаревших и непригодных к употреблению пестицидов.
• Организовать периодическую инвентаризацию складов хранения запрещенных и непригодных к употреблению продуктов защиты растений и на этой основе дать экспертную оценку действительного состояния и их количества в складах.

• Собирать и рассматривать разработанные общинами проекты сбора и сохранения запрещенных и непригодных к употреблению пестицидов. Для этой цели были изготовлены типовые проекты.

• Разработать основные критерии для оценки и одобрения проектов это: состояние склада, количество и вид пестицидов в нем, удаленность от населенных мест, близость источников водоснабжения, высота уровня грунтовых вод, отстояние от защищенных зон, собственность склада и пр.

МОСВ одобрило два способа хранения — базовые склады и железобетонные контейнеры.

Основная цель была свести до минимума количество мест хранения и складирования ответственного хранения запрещенных и непригодных к употреблению пестицидов, при полном соблюдении и гарантировании экологических, здоровьесохранительных и других нормативных требований.

В 2000 году был выполнен пилотный проект “Уничтожение рисковых пестицидов из Болгарии в Голландию” организован и финансирован Министерством окружающей среды и вод. По этому проекту было вывезено 30 тонн особенно опасных пестицидов (содержащих ГХЦГ - гексахлорциклобензен и ДДТ - дихлор-дифенил-трихлорэтилен). Эти пестициды были собраны из районов Софии, Пловдива, Шумена и Бургаса и были уничтожены в инсинераторе в городе Роттердам.

С 1999 по 2004 год были освобождены и санкционированы (проведена детоксикация) 783 складов хранения, содержащих запрещенные и непригодные к употреблению пестициды, что составляет 61.7% из общей численности складов, установленных инвентаризацией в 1997 году.

К декабрю 2004 года мониторинг состояния непригодных к употреблению (запрещенных и с истекшим сроком годности) пестицидов показал следующее:

Были определены 73 базовые склады, где ненужно сохраняются и хранятся пестициды — 2 321.8 тонн твердых (порошкообразных), 412 786 литров жидк и 541 куб. метров смешанных; были заполнены 1364 железобетонных контейнеров и таким образом освободились 783 складов хранения.

Для обработки остаются еще 485 складов, содержащих непригодные пестициды. В них имеется 1 924.8 тонн твердых (порошкообразных), 591 355 литров жидк и 6 381 куб.миров смешанных,

| Число освобожденных и санированных складов по годам: |
|-----------|-----------|-----------|-----------|-----------|-----------|
| Год       | 1999 | 2000 | 2001 | 2002 | 2003 | 2004 |
| Число складов | 121 | 129 | 108 | 135 | 178 | 112 |

Число железобетонных контейнеров, заполненных непригодными пестицидами по областям к декабрю 2004 года

В некоторые области нашей стране непригодные к употреблению пестициды собраны целиком и полностью в железобетонные контейнеры или в базовые склады и этим образом они находятся под эффективным контролем и не угрожают загрязнением окружающей среды и здоровью людей, животных и птиц. Такими областями являются:
Габрово, Смолян, Русе, София-город и Ямбол.
Второй этап программы включает строительство установок (инсектициидоров) для высокотемпературного уничтожения пестицидов, собранных в базовых складах и депонированных в железобетонных контейнерах. Этот этап является приоритетом Министерства охраняющей среды и вод.
Согласно Директиве о средствах защиты растений (Выпуск пестицидов на рынок, 91/414 ЕС) [6] при разрешении продуктов защиты растений необходимо иметь достаточно доказательств для того, что при их правильном приложении для достижения определенной цели, они являются достаточно эффективными и не вызывают нежелательных эффектов на растения и окружающую среду и вредных эффектов на здоровье человека и животных или на подпочвенные воды.
В середине 80-ых годов рабочая группа по продуктам защиты растений Европейской организации защиты растений поставила перед собой целью разработать концепцию о правильном и целесообразном приложении продуктов защиты растений в зависимости от условий в отдельных странах—членах Европейской организации защиты растений. Эта концепция должна представлять собой серию рекомендации по оптимальному приложению продуктов защиты растений для каждой культуры, в зависимости от специфических вредителей и болезней. В результате этого в 1993 году были разработаны основные принципы “Надлежащей растительно-защитной практики” (Good Plant Protection Practice), которые в 2002 году были актуализированы и доработаны. На основе этого, в марте 2004 года в Республике Болгарии тоже были разработаны и приняты общие принципы “Надлежащей растительно-защитной практики”. С этими общими принципами познакомились все специалисты региональных служб защиты растений по областям.
Концепция о “Надлежащей земледельческой практике” (Good agriculture practice) при употреблении продуктов защиты растений декларирована на кодекс Комитета по остаткам пестицидов: “рекомендуемое, одобренное или разрешенное на национальном уровне безопасное применение пестицидов в реальных условиях на каждом этапе производства, сохранения, транспортирования, распространения и переработки пищевых продуктов и кормов для животных, необходимое для осуществления эффективного и надежного контроля над вредителями и болезнями. Безопасное применение пестицидов охватывает ряд условий приложения, достигая самого высокого - рекомендуемое, одобренное или разрешенное применение на национальном уровне. В этом контексте, “безопасное применение” принимает во внимание общество здоровье, охрану окружающей среды и минимум количества для эффективного контроля над вредителями и болезнями, их использование предусмотрено таким образом, что уровни остаточных количеств будут иметь возможно самые низкие величины.
Национальная служба защиты растений разработала принципы “Надлежащей растительно-защитной практики” (GPPR) для основных сельскохозяйственных культур (зерновые злаковые, зерновые бобовые, масличные, овощные, плодовые - сеяное и косточковые культуры, виноград, плодовые ягодные - малина, клубника, черная смородина). Предоставляет утверждение и обучение сельскохозяйственных производителей их применению.
Для создания необходимых условий для введения требуемой документации и улучшения контроля со стороны Национальной службы защиты растений за применением средств защиты растений и за употреблением удобрений в сельскохозяйственном производстве и на основании закона защиты растений в 2002 году был одобрен Приказом Министра земледелия и лесов “Надежных проведенных химических обработок и употребления удобрений, почвенных добавок и биологически активных веществ”. Национальная служба защиты растений разработала указания по порядку заполнения “Надежная”. Периодически эксперты Региональных служб защиты растений по областям делают проверки на правильное ведение “Надежная”. Следят какие продукты защиты растений употребляются и соблюдаются ли зарегистрированные дозы приложения, в соответствии с ежегодного издания Национальной службой защиты растений “Список разрешенных для выпуска рынка и употребления продуктов защиты растений, зарегистрированные удобрения и почвенные добавки”.

Литература
5. Базельская конвенция, Госуд. Газ. № 1/3.01.1997.
OVERVIEW

Georgia has signed the Stockholm convention in 23.05.2001 and has not ratified it yet. The work on ratification is currently in the process.

The country is very committed with the solution of obsolete pesticides and PCB problems and is in full swing with the works for the National Implementation Plan now.

The government started to implement NIP with UNDP Country Office in 2003 and is still in the process of inventorying the contaminated sites and identifying the sources of POPs throughout Georgia.

In this paper I will try to share our gained experience during project implementation process.

Financing Agencies of the Preparation of the POPs NIP under the Stockholm Convention Project:
1. GEF;
2. Government of Georgia - Ministry of Environmental Protection and Natural Resources of Georgia.

Main Goals of the Project:
1. To create sustainable capacity in Georgia to meet obligations under the Stockholm Convention;
2. To Prepare NIP on POPs in Georgia;
3. To advise the Government of Georgia to ratify the Convention and assist in developing and producing the relevant information for the ratification process.

Fields the Project has been Studying:
1. Technical Topics- PCBs, Unintentional Products, Pesticides;
2. Legal Basis;

Project Structure:
1. National Project Director;
2. Project Manager;
3. Coordinator of Experts in PCB, Unintentional Products, Pesticides;
4. Legal Expert;
5. Public Awareness Expert;

Inventory Structure:
1. Regional Representation in 14 regional Offices;
2. Representatives from the directly involved agencies for the POPs issues:
   • Ministry of Environmental Protection and Natural Resources;
   • Ministry of Agriculture and Food;
   • Ministry of Health and Labor;
   • Ministry of Energy.

Most of these agencies were directly connected with POPs. They are regulating and coordinating bodies of the Government. It was purposely done to invite representatives from those agencies and to create inspecting/inventorying groups in regions. Since the detailed inventory was planned to be undertaken, the project decided to get the regional representatives from those agencies involved in the inventory process taking into account that persons living in the regions and working on the problem would deliver the comprehensive and valuable data about the storages, amount and places of the Pesticides and Transformers there. Doing it we also left and increased the capacity to inspect, increased the regional inspectors awareness about the POPs and related problems. It was a right decision which could be used as a good practice.

In Brief, Regional Working Groups were responsible:
1. To study the state of the Region;
2. To fill the forms in (FAO, UNEP);
3. To take PCB & Pesticide Samples.

Laboratories Assessment:
1. One of the main goal was to build or strengthen the existing capacity of the Lab;
2. To arrange the Lab meeting;
3. To distribute Questionnaires;
4. To assess the capacity.
Assessment of the Laboratories became time consuming process. Since we invited all Laboratories, we gave the presentation about the goal of the project and handed out the specially developed questionnaires to be filled in. Submitted filled-in questionnaires were studied and screened. The second phase was to visit the short listed Labs in order to have better understandings on their capability to provide services for the project.

There were several samples and samples testing made.

PCBs/Pesticides/Unintentional Products– Related Conditions:
1. Insufficient/dispersed statistical data;
2. Inadequate legal basis;
3. No analytical basis and monitoring system;
4. No state POPs management strategy.

The data we were looking for either were dispersed or absent. Project decided to deal with this problem by gathering it - compiling and double checking with Producers and with Users. We believe that the data that have been gener-
ated are reliable and optimized.

The legal framework assessment was an interesting and creative process. We assessed and overviewed the existing regulations and normative acts. We have developed precise recommendations in order to identify what kind of amendments to be made in the Georgian legislation pertaining for regulation of POPs.

The main problem related to these issues stated above were the discrepancies in the existing legislative framework and therefore we recommended undertaking amendments safeguarding clear delegation of the responsibilities among relevant state agencies.

**Pesticides/PCBs/Unintentional Products – Inventory Scales:**

1. PCBs: All 14 regions of Georgia
   - Energy sector
   - Metallurgy
   - Chemical industry
   - Wood and cellulose/paper industry
   - Oil processing
   - Food sector

   More than 15,000 transformers
   More than 5,500 capacitors and 3,200 high-voltage converters.

**Transformers:**

Up to date, total of 15,757 transformers have been registered by the project experts and regional inspectors. The brief description of the size and company-belonging of most of these follows:

- Power generation: 90 large size transformers, out of which 80 are of USSR make and remaining 10 originating from various countries. Some of the transformers originate from the first half of the 20th century.
- High-voltage power transmission network: The national high voltage network contains 458 substations with 4-5 transformers each. The total number is hence around 2000. A detailed list of type, make and year of manufacture is available with the project experts.
- The low-voltage distribution system is managed by 4 entities. The biggest is Georgian Distribution Company, covering all regions of Georgia apart from Kakheti, Adjara and Tbilisi. This company has 9,411 transformers of different effect levels in its distribution network. The details of this equipment are available to the project experts. The same applies for the around 2,000 transformers in the Tbilisi (Telasi) network, ~1,200 transformers in Kakheti, and 2,000 in Adjara.

**Railways:** 5 regional departments have 58 substations with 4-5 transformers totaling in 300 transformers. These have been inspected at site and detailed data are available for these as well as for the transformers in the Tbilisi metro system.

**Mills:** 15 including the major units involved in milling different agricultural crops have been included in the survey. Here some 60 transformers have been accounted for.

The survey has relied on questionnaires and inspections for obtaining the presented numbers. Altogether, the survey on PCB containing equipment has obtained data from some 400 big and medium sized companies out of a total of 840 functioning industries. It is estimated that this amounts for some 80% of the total industrial activity in the country.

**Capacitors and converters:**

According to the survey covering both energy sector and the main industries in 12 regions of Georgia (excluding Racha and Kvemo Svaneti/lechxumi, where the data on synthetic oil-containing equipment are close to zero) total of 5,460 capacitors of 25 types have been registered up to date. Out of these, ~1,100 are still functioning, while ~4,400 are out of order. The total mass of the equipment (including oils and casing) is estimated to be ~295 tons, and the estimated mass of oils only ~95 tons.

The number of converters registered is ~3,200.

**Pesticides:**

- Agriculture
- Health Protection
- More than 200 sites
- Hundreds of tons of unknown pesticides (357 tons of obsolete pesticides at different sites plus 2,700 tons at Jagluji landfill).

Total of 214 sites have been checked in 12 regions of Georgia, out of which at 46 sites the contamination by pesticides was reported. Roughly estimated total amount of pesticides discovered is ~357 tons. 71 samples of unknown chemicals and 11 samples of contaminated soils have been taken by the regional inspectors and were transferred to the laboratory. The lab has performed qualitative and quantitative analysis of the samples on POPs.

The summary of the sample analysis looks as follows: out of 71 samples of unknown chemicals, 47 contain at least one of the POPs (~66% of the total number). All 11 samples of contaminated soils bear the trace of few POPs. The main contaminants are hexachlorocyclohexane (benzene hexachloride), heptachlor, DDT and its derivatives.

**Unintentional Products**

Contamination of the environment in Georgia by dioxin-furans reduced 3.019 times from 1990 to 2004 (from 290.007 to 96.056 g TEQ/a).

**UNEP Guidelines (Discrepancies/Suggestions):**

Following guideline literature was used by the technical experts during the inventory process:

4. The national project on assessment of management infrastructure for chemicals (UNITAR).

The PCB experts have following suggestions for improving the existing guidelines:

- Low voltage (small) transformers – more probability of PCB high concentrations
- High voltage transformers – lower probability of high concentrations
- Direct relations with transformer-capacitor-industries
- Need of Full catalogue of the labels for capacitors.
COPING WITH STOCKPILES OF OBSOLETE CROP PROTECTION PRODUCTS IN SLOVAKIA

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INTRODUCTION

As in almost all of the countries whose economies were centrally planned and governed, stockpiles of obsolete crop protection products have accumulated in large-scale production units, such as state-owned and co-operative farms throughout Slovakia. This was mostly due to malfunction of supply/demand system. After the shift in socio-economic relations in early 1990s, ownership rights to property in agribusiness used to change even several times, very often resulting in lost records in respect of chemicals commonly used in agricultural production and stored in the premises. Stockpiles of obsolete crop protection products were thus gradually emerging and present-day agribusiness companies and entities of various nature bear their ecological burden that at the time being has no “owner”. The current economic situation in the most of Slovakian agribusiness does not allow the companies to manage the problem by themselves.

ESSENTIAL OBJECTIVES

Therefore a common Project has been elaborated by several entities with two essential aims - to dispose of the ecological impact presented by obsolete and expired crop protection products and to prevent possible ecological disasters that may emanate from either the current situation or from incorrect decisions made, as regards coping with it.

Apart from this, two more issues are deemed important. For future sound development in this field it is necessary that excessive stockpiling of unused crop protection products be prevented and that schemes for both unused crop protection products, if any, and emptied, non-recyclable containers be built up.

HISTORY OF THE PROJECT

Common joint efforts were made by

• MP SR, under whose auspices the Project was elaborated,
• NRL UVL, which has partly backed the technical aspect for the disposal,
• ÚKSÚP as the national administration body having kindly provided field information and data through their phytosanitary inspectors, and last, but not least,
• SCPA as a non-profit association of certain stakeholders and serving as the Project Manager.

First inventory was made from the initiative by ÚKSÚP, whose phytosanitary inspectors as first-line field staff were requested to conduct a survey in respect of unusable crop protection products. This initial step was made in June 2000; phytosanitary inspectors made their off-time work and managed to record some 156 tonnes in approximately 60% of stores at farms. This time they encountered various attitudes from owners of stockpiles, extending from co-operation to open rejection to provision of requested data.

A second, more detailed, survey was completed in March 2003, which resulted in some 306 tonnes of unusable crop protection products being documented. It was commissioned as a result of findings of a DG (SANCO) 8694/2002 mission to Slovakia carried out by FVO Dublin in October 2002, whereby Slovakia was invited to conduct a new inventory of obsolete crop protection products, this time including also POPs. The result of the second inventory was better, as phytosanitary inspectors instructed end users and official records with breakdown of findings were made. Phytosanitary inspectors managed to visit 98% of all known stores at agribusiness entities.

The revealed amount was 306 tonnes of obsolete and expired crop protection products, of which 9.7% are those listed as POPs under the Stockholm Convention. However, this number is still not considered definite and our estimation may be 1/3 more, i.e. around 400 tonnes. The overall breakdown is approximately 40% (expired approved crop protection products), 30% (obsolete crop protection products with the above POPs included) and 30% (unidentifiable agricultural chemicals, probably mostly crop protection products). The estimated increase does not include recorded crop protection products on farms and also those possessed by non-professional users, who will be involved in the Project as well.

The quantities stored at individual farms varied from 20 g to 8 tonnes and consist of more than 602 of various pesticides. Fortunately no plant protection products stockpiled in open-air landfills have yet been found. However, the standard of their storage varies from safe stores complying with the requirements as laid down by the relevant regulations, to those in a sorry state. These latter are fortunately only rare extremes, usually remotely located and may be on the verge of ecological disaster under unfavourable force major circumstances. They used to be owned by entities with no clear ownership and business motivation. As regards POPs, the last one (heptachlor) was banned from use in 1989 but was still produced in the former Czechoslovakia.

The Project referred to in this paper was designed in October 2004; however, no financial means have been available to launch it so far.

The activities made by NGOs should be mentioned, too. In Slovakia Ipelská únia is active in this field; they have...
made a lot of good work and are certainly willing to participate in the Project. Their activity may be seen in the proceeding from the most recent HCH forum held in Ukraine. The attitude of Greenpeace is more disputable, though their making the general public aware of the problem may be well meant.

ALTERNATIVE SOLUTIONS

A brain storming was made to assess the three following alternative solutions, for each of them its pros and cons were thoroughly considered and a SWOT analysis was made as well.

“Safe” storage

This way of coping with obsolete crop protection products cannot be considered a genuine disposal as the problem remains and is continuously pushed ahead. No “safe” landfills with their limited storage capacity, limited ability to resist force majeure events and unlimited ability to attract “undesirable” attention can be built. The operation of the present day landfills is re-considered. Numerous experiences with the storage of comparable (e.g. radioactive) waste have shown that hitherto no totally safe containers made of high quality and corrosion resistant materials for a reasonable price exist. In our opinion, use of this solution is very disputable to prevailing conditions of Slovakia. The country is densely populated and serves as an important source of potable water reserves, also for its neighbours downstream. The most recent experience with water contaminated with heavy metals and running out of former mines, indicates hidden risks in such a solution. “Safe” storage is forced through by some NGOs even though only to serve as a temporary solution before a non-incineration technology is invented or installed. It may be, but at what price? We have to bear in mind that the costs of running a “safe” landfill full of hazardous waste is a never ending story.

NON-INCINERATION TECHNOLOGIES

We must take into account that non-incineration technologies may be available worldwide, but alas not yet in Slovakia. The elimination of dangerous chemicals using non-incineration procedures may be true for cases when exactly and well known products are to be destroyed with thoroughly sophisticated, specific and controlled technologies. But we shall also be aware of the urgent need to dispose of almost 400 tonnes of dangerous waste, consisting of more than 602 active substances, additives, solvents, etc.

However, we admit that this way of destruction is available and suitable for those 9.7% mentioned above. But what to do with the remainder formed by supposed 306 tonnes of “mixed” stockpiles of unusable crop protection products? Costs of running non-incineration destruction technologies are in no way single, though not “eternal”. Moreover, these technologies will surely demand new investments to build up “safe” sites for collection, temporary (or better said “eternal”) storage and sorting of hazardous waste with all the risks that are inherent to “safe” landfills.

INCINERATION

After having considered all three options, we have come to the conclusion that incineration is the best way to get rid of the stockpiles of obsolete and expired crop protection products in Slovakia.

First, we must eliminate the said ecological burden as quickly and painlessly as possible. Regarding the operation capacity of the incineration plant mentioned below this is feasible.

Second, costs related with the collection, i.e. transport of dispersed unusable crop protection products into the incineration plant are the same as for the two aforesaid alternative solutions.

Third, hazards inherent to the transport are the same, as waste must in any case be transferred, whether to a common landfill or to another type of facility. For this latter a mobile plant was not considered, but still certain quantities must be accumulated (transported and stored) to feed it as required. Hazards inherent to the temporary storage at an incineration plant are limited to its capacity.

Fourth, incineration plants are “versatile destructors”, therefore no waste-specific technologies are needed and they may serve as terminal destinations for (not only) plant protection products remnants and non-recyclable containers in the future as the Projects intends.

Fifth, the incineration process is controllable and may still remain subject to adaptation to technological progress.

INCINERATION PLANT FECUPRAL VEL’KY SARIS

The plant is located in eastern Slovakia, in the vicinity of Prešov, has been operating since 2000 and is the only accredited incineration plant of this type in Slovakia, complying with requirements as laid down in (Slovak) Act No.223/2001 on Waste and Directive 2000/76/EC on the incineration of waste. In November 2002 it was visited by a DG (SANCO) 8694/2002 mission.

The waste to be destroyed may be solid, liquid or of a paste-like consistency. Waste must be homogenised immediately before feeding. Its incineration capacity is 3.6 tons per 24 hours with two-stage incineration in a rotary oven at (500-900 °C) and then in a finalising chamber equipped with a thermoreactor (at least 1200 °C). Organic compounds are broken down in the thermoreactor during a retention time of 2 - 3 s. Natural gas (75 m³ h⁻¹) is used as stabilising fuel. Exhaust fumes are dry cleaned.

First, absorbing agent is dispersed into the stream of fumes, which passes a tissue filter. Absorbent is a mixture of sodium hydrogencarbonate and activated carbon. Certain part of halogenated compounds, including PCDD/F, and heavy metals are removed from the stream here.

Second filter filled in with a special brown coal-coke serves to capture dioxins. The plant has its own transportation units for ADR operation.

A BRIEF DESCRIPTION OF THE PROJECT

The Project is envisaged to last for two years, from its launching with a collection scheme for both eventual remnants of unused crop protection products and non-recyclable containers as its outputs.
Stage 1
A detailed review, verification and updating of the list of unusable crop protection products. Conclusion of necessary contracts. Other arrangements.

Stage 2
Scheduling the collection, transportation and destruction of unusable crop protection products intended for incineration.

Stage 3
Collection, transportation and destruction of unusable crop protection products according to the above schedule.

ORGANOCHLORINATED PESTICIDES (OCPS) IN THE CZECH REPUBLIC

PART I. ASSESSMENT OF THE HISTORICAL PRODUCTION, USE, IMPORT AND EXPORT AND OBSOLETE STOCKS

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PRODUCTION OF OCPS

The two largest pesticide producers in the former Czechoslovakia were Spolana Neratovice and Juraj Dimitrov Chemical Manufactory (CHZJD). The history of the national production of persistent organochlorinated pesticides began in 1950 after the completion of research on the synthesis of DDT by the Scientific Institute of Agrochemical Technology in Bratislava. A year later, conditions were created for the mass production of technical HCH. Since 1959 (according to some sources since 1956) only pure lindane (> 99 % g-isomer of HCH) was used in agriculture and its use was limited to seed treatment (flax, rape).

Technical HCH, however, was still used in forestry. At the beginning of the sixties, the first cases of resistance towards DDT were demonstrated (Colorado potato beetle, Leptinotarsa decemlineata), and later in various other types of insects (for example, rape blossom beetle, Meligethes aeneus).

After these discoveries, the production of DDT faltered and its usage was substituted first with kelevan (also a chlorinated substance), and later with chlorphenvinphos and carbamates. Unused reserves were stored in the 1950s and 1960s in individual agricultural co-operatives and in Agricultural commercial and supply manufactories (ZZNZ) – not only DDT, but also other pesticides. Gradually it became necessary to begin to regulate the liquidation of these unused and unusable supplies of OCPS.

REGISTRATION

At the end of the 1960s and especially in the 1970s, the usage of OCPS was gradually restricted and banned and these substances were gradually substituted by other types of effective chemical substances. The steps leading up to this were:

- The application of these substances against harmful organisms and the replacement of methods such as seed treatment or application during seeding;
- Replacement of DDT by organophosphates, carbamates, pyretoxids and growth regulators;
- Regulation and ban of the use of polycyclic chlorinated insecticides such as aldrin, dieldrin and heptachlor; restriction of the use of endrin to the liquidation of field mice (field mouse Microtus Arvalis) when approved in each special case of use, and restriction of the large-scale use of fungicides based on HCB (hexachlorobenzene) and PCNB (pentachloronitrobenzene) for use against blight.

As far as produced quantities are concerned, only a small portion of the data is accessible. The estimation of the production in the former Czechoslovakia is shown in Table 2.

Information concerning technical HCH also includes data about lindane production. In total, 3 330 t of lindane were produced, that is about 5% of the production of technical HCH, even though at the beginning of production it was less than 2% (in the year 1958, 460 t of technical HCH, and 7 t of lindane were produced), while towards the end of production, the production of lindane was around 10% (in 1976 2 390 t / 223 t g-isomer). This means that the use of technical HCH in various preparations was fairly high, especially at the beginning of production, and then decreased. Also data regarding trichlorobenzene (side product after the lindane isolation process) is accessible, and allows for a rough estimation of how much technical HCH was used. Figure 1 shows a graph of the development of the production of technical HCH in comparison to lindane and trichlorobenzene; the graph shows how technical HCH was thenceforth used, despite the beginning of lindane production.
Table 1. Historical profiles for chlorinated pesticides registered in the former Czechoslovakia

<table>
<thead>
<tr>
<th>Active substance: Preparation (content of active substance)</th>
<th>Formulation / Producer</th>
<th>Registered from - to</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aldrin (not available)</td>
<td>P /</td>
<td>1962 - 1963</td>
<td></td>
</tr>
<tr>
<td>DDT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerosol DDT (10 %)</td>
<td>K / Spolana</td>
<td>1958 - 1973</td>
<td></td>
</tr>
<tr>
<td>Aerosol DL (2.5 %)</td>
<td>K / Spolana</td>
<td>1960 - 1973</td>
<td>Lindan 1 %</td>
</tr>
<tr>
<td>Antrix (15 %)</td>
<td>EC (?) / Spolana</td>
<td>Not available, at least until 1975</td>
<td>Lindan 7 % in forestry</td>
</tr>
<tr>
<td>Cyclodyn (3.75 %)</td>
<td>P / CHZJD</td>
<td>1955 - 1958</td>
<td>Technical HCl 2.5 %</td>
</tr>
<tr>
<td>Dibovin (10 %)</td>
<td>P / not available</td>
<td>Not available</td>
<td>Disinfectant for habitation, livestock, stables</td>
</tr>
<tr>
<td>Duaryl (69 %)</td>
<td>SC / not evaluated</td>
<td>Not available</td>
<td>Probably only developed, was not used</td>
</tr>
<tr>
<td>Dyk (50 %)</td>
<td>DP / Spolana</td>
<td>1959 - 1973</td>
<td></td>
</tr>
<tr>
<td>Dynocid (5 %)</td>
<td>P / CHZJD</td>
<td>1951 - 1973</td>
<td></td>
</tr>
<tr>
<td>Dynol (20 %)</td>
<td>DKV / Spolana</td>
<td>1955 - 1969</td>
<td></td>
</tr>
<tr>
<td>Gamodyne (3 %)</td>
<td>P / CHZJD</td>
<td>1957 - 1973</td>
<td>Lindan 0.5 %</td>
</tr>
<tr>
<td>Holus (not available)</td>
<td>In solvents non-miscible with water / not available</td>
<td>Not available, used at least until 1962</td>
<td>p-dichlorobenzene used in stables, textile stockrooms, workshops</td>
</tr>
<tr>
<td>Ipsotox (2.5 %)</td>
<td>S / Spolana</td>
<td>Not available, used at least until 1972</td>
<td>HCH techn. 8 % in forestry</td>
</tr>
<tr>
<td>Ipsotox Special (2.5 %)</td>
<td>S / Spolana</td>
<td>New 1972</td>
<td>Lindan 1 % only in forestry</td>
</tr>
<tr>
<td>Meryl N (2 %)</td>
<td>Not available / Spolana</td>
<td>New 1972</td>
<td>Pentachlorophenol 3 %; only for impregnation of wooden surfaces</td>
</tr>
<tr>
<td>Lidyk (46 %)</td>
<td>DP / Spolana</td>
<td>1959 - 1973</td>
<td>Lindan 4 %</td>
</tr>
<tr>
<td>Neradititin (10%)</td>
<td>P / Spolana</td>
<td>Not available, used at least until 1969</td>
<td>Human hygiene</td>
</tr>
<tr>
<td>Nera-emulze (30 %)</td>
<td>Emulsion / Spolana</td>
<td>Not available, used at least until 1964</td>
<td>Human hygiene</td>
</tr>
<tr>
<td>Nerafum (40 %)</td>
<td>FK / Spolana</td>
<td>Not available, used at least until 1964</td>
<td>Human hygiene</td>
</tr>
<tr>
<td>Nerakain (30 %)</td>
<td>EC / Spolana</td>
<td>Not available, used at least until 1964</td>
<td></td>
</tr>
<tr>
<td>Pararyl (not available)</td>
<td>Not available</td>
<td></td>
<td>Probably only developed, was not used</td>
</tr>
<tr>
<td>Pilus (10 % DDT)</td>
<td>Not available</td>
<td>Not available</td>
<td>In grain silos; combined with grains</td>
</tr>
<tr>
<td>Pentalidol (2 %)</td>
<td>S / Spolana</td>
<td>Not evaluated; many years before 1972, continued at least until 1975</td>
<td>Pentachlorophenol 5 %, lindan 0.1 %; only for impregnation of wooden surfaces by coat of paint</td>
</tr>
<tr>
<td>Solomitol</td>
<td>Water soluble liquid / not available</td>
<td>Not available, used at least until 1962</td>
<td>Similar to Pentalidol</td>
</tr>
<tr>
<td>Tridynol (20 %)</td>
<td>Not available</td>
<td>Not available</td>
<td>In oil; in empty grain silos</td>
</tr>
</tbody>
</table>
# Dieldrin

<p>| | | | |</p>
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<tr>
<th></th>
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<tbody>
<tr>
<td>Alvit % (90 %)</td>
<td>MP</td>
<td>1960</td>
<td>1968</td>
</tr>
<tr>
<td>Dieldrex B (75 %)</td>
<td>MP</td>
<td>1962</td>
<td>1968</td>
</tr>
<tr>
<td>Coating preparation (9 %)</td>
<td>MP</td>
<td>1965 - 1968</td>
<td></td>
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# Endrin

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<tbody>
<tr>
<td>Endrin 20 (20 %)</td>
<td>EC</td>
<td>1960 - 1983</td>
</tr>
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# HCH technical

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<tr>
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<tbody>
<tr>
<td>Cyclo-HCH (10 %, min. 1 % gamma)</td>
<td>P / Spolana, also CHZJD</td>
<td>1952 - 1970</td>
</tr>
<tr>
<td>Cyclo or Cyclo Powder (10 %)</td>
<td>P / CHZJD</td>
<td>Not available, used at least until 1972</td>
</tr>
<tr>
<td>Forst-Nexen (18 %, 75 % gamma)</td>
<td>EC / FRG</td>
<td>Not available, used at least until 1975</td>
</tr>
<tr>
<td>Ipsotox (8 %)</td>
<td>See DDT</td>
<td>See DDT</td>
</tr>
<tr>
<td>Cyclodyn (2.5 %)</td>
<td>See DDT</td>
<td>See DDT</td>
</tr>
</tbody>
</table>

# Heptachlor

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<tbody>
<tr>
<td>Agronex Hepta T 30 (29 %)</td>
<td>MP / Celamerck / (FRG)</td>
<td>1970 - 1985</td>
</tr>
</tbody>
</table>

# Chlordane

<p>| | | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>TMD 30 %</td>
</tr>
</tbody>
</table>

# Hexachlorobenzene

<p>| | | |</p>
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Agronol H (10 %)</td>
<td>MP</td>
<td>1961 - 1977</td>
</tr>
<tr>
<td>Hexachlorobenzene (25%)</td>
<td>P</td>
<td>Up to 1977</td>
</tr>
<tr>
<td>HCB (90 %)</td>
<td>DP</td>
<td>1959 - 1977</td>
</tr>
</tbody>
</table>

# Methoxychlor

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Methoxychlor (10 %)</td>
<td>P / Spolana</td>
<td>1965 - 1972</td>
</tr>
<tr>
<td>Methoxychlor (25 %)</td>
<td>EC / not available</td>
<td>1965 - 1972</td>
</tr>
<tr>
<td>Methoxychlor Aerosol (15 %)</td>
<td>K / not available</td>
<td>1965 - 1972</td>
</tr>
</tbody>
</table>

# Mirex

<p>| | | |</p>
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TMD 30 %</td>
</tr>
</tbody>
</table>

# Toxaphene

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Toxaphene (10 %)</td>
<td>P / not available</td>
<td>1958 - 1960</td>
</tr>
<tr>
<td>Melipax (10 %)</td>
<td>P / VEB Fahlberg-List (GDR)</td>
<td>1961 - 1962</td>
</tr>
<tr>
<td>Melipax 60 EC (60 %)</td>
<td>EC / VEB Fahlberg-List (GDR)</td>
<td>1961 - 1983</td>
</tr>
</tbody>
</table>

**Legend:**
- DP - dispersed powder
- DKV - dispersed liquid concentrate for dilution with water
- EC - emulsion concentrate
- K - liquid concentrate for application without diluting
- MP - dispersed powder for seed treatment
- P - powder
- S - solution
- VT - fumigation tablets
- Grey items = used in communal hygiene or for livestock disinfection
Concerning the export of persistent organochlorinated pesticides, no usable data was obtained. From accessible information, it is apparent that the need for plant protection demanded the import of specific substances, but export, especially at the beginning of production, was very low, if any. The exception is the period when semi-operational production of DDT and HCH was established, and these pesticides were exported to North Korea during the time of the Korean War. Regarding the export of organochlorinated pesticides, contrary to other types of pesticides, there was never any demand for them.

The assessment of imported pesticides shows that in the 1970s no preparation with an organochlorinated base was imported. There was no change even towards the end of the 1970s, when a range of active substances for the preparation of various pesticides began to be imported, but with none having an OCP base.

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It is therefore possible to state that the most significant import concerned with some of the POPs was the import of toxaphene, and its preparation Melipax from the former DDR.

Concerning the frequency of application, it is, of course, dependent on its method. In most cases and for most pesticides, the dose of active substance was between 0.5 and 1.5 kg ha\(^{-1}\), but in some cases it could have been applied in an amount outside this range. For example, recommended Aerosol DDT doses were 6 l ha\(^{-1}\), which corresponds to 3.6 kg ha\(^{-1}\) of active substance. The recommended dose of Cyclo Powder was 40 kg ha\(^{-1}\), which corresponds to 6.4 kg ha\(^{-1}\) of active substance, i.e. g-HCH, and the recommended dose of hexachlorobenzene (used for soil disinfection) was 50 kg corresponding to 12.5 kg ha\(^{-1}\) HCB. On the other hand, in the case of endrin 20, the recommended dose was 0.5 l ha\(^{-1}\), which corresponded to only 0.1 kg ha\(^{-1}\) of active substance, but endrin is a very special case. Expert estimates state that the consumption of pesticides per hectare of agricultural land in the Czech Republic is around 1 kg ha\(^{-1}\), but in the 1960s was around 4 kg ha\(^{-1}\), if not more.

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**OBSOLETE STOCKS, UNUSED RESERVES**

Obsolete pesticide stocks were in part liquidated in the 1960s and 1970s, mainly by combustion, while the remainder had often been stored under inappropriate conditions with the strategy of postponing their liquidation until a suitable liquidation method was found. Because these obsolete reserves were often stored without maintaining any type of security precautions, they represented a significant source of danger for environmental contamination.

It was not until after 1989 that suitable liquidation of these old reserves began with the help of appropriate technology. The first portion was incinerated in Ingolstadt (FRG). According to documentation, this included 1 900 tonnes of pesticides or pesticides containing waste, of which 50 to 60 % were POP pesticides (in most cases DDT and HCH).

In 1992 at the State Plant Protection Administration (SOR) Prague, a computer program named „Přípravky“ was acquired to document the preparation for the liquidation of unused pesticides. Its database contained approximately 1 700 records. One record contained information about the region, the district, the preparation, the company, the form...
Table 4. An overview of the obsolete pesticide stocks liquidated in 1993

<table>
<thead>
<tr>
<th>Preparation</th>
<th>Amount [kg, l]</th>
<th>Preparation</th>
<th>Amount [kg, l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclon</td>
<td>125</td>
<td>Hermaí</td>
<td>5 300</td>
</tr>
<tr>
<td>Cyklidón</td>
<td>71</td>
<td>Hexanál</td>
<td>404</td>
</tr>
<tr>
<td>Desfril</td>
<td>192</td>
<td>Lidénal</td>
<td>3 697</td>
</tr>
<tr>
<td>DDT</td>
<td>2 104</td>
<td>Lidykol</td>
<td>837</td>
</tr>
<tr>
<td>Dynacit</td>
<td>24 918</td>
<td>Linán</td>
<td>61</td>
</tr>
<tr>
<td>Dykrol</td>
<td>286</td>
<td>Meligaas</td>
<td>12 581</td>
</tr>
<tr>
<td>Gamacid</td>
<td>1 451</td>
<td>Neradit</td>
<td>33</td>
</tr>
<tr>
<td>Gamadón</td>
<td>33 008</td>
<td>Míšel</td>
<td>18 699</td>
</tr>
<tr>
<td>Gesareol</td>
<td>300</td>
<td>Other</td>
<td>733</td>
</tr>
<tr>
<td>HCH</td>
<td>560</td>
<td>Total</td>
<td>105 479</td>
</tr>
</tbody>
</table>

of preparation, the amount, the chemical substance, and the state of its encasement. The information was received by workers in the regional and district SOR - the information was from the Ministry of Agriculture.

SOR documented a total of 584 100 kg (1) of obsolete pesticide residues. Stocks declared by agricultural companies in 1991 to the regional and district SOR workers were included in this amount. The true amount was probably higher, because the database did not include all agricultural organisations and private agriculturists possessing such stocks.

Despite all attempts to decrease the amount of obsolete stores in 1992 (combustion in England), actual liquidation of selected groups of obsolete pesticides did not occur until the second half of 1993. This liquidation became possible thanks to the generous subsidy policy of the Czech Ministry of Environment for the export of hazardous wastes. This included mainly pesticide residues based on DDT and HCH, which were taken over from agricultural entities by the firm AGRIO in Mišice. A portion of the pesticide stocks in the form of powder was exported to the incinerator at GSB Ebenhausen in Bavaria (paid for by the Czech Ministry of agriculture) by the firm EKO-AQUA-QUELLE. Other obsolete pesticide stocks were either liquidated in incinerators or were disposed of at dumping sites for hazardous waste in the Czech Republic.

The chemical substances chosen were those which were eligible for subsidies from the Czech Ministry of Agriculture. An overview of the obsolete pesticide stocks liquidated in 1993 is shown in Table 4.

CHLORINATED PERSISTENT PESTICIDES IN WASTES

Besides polychlorinated biphenyls (PCBs), and substances which arise as undesirable products during some technological processes or waste processing (HCB, PCDDs, PCDFs), the most significant group of persistent organic pollutants subject to ban or restrictions are persistent chlorinated pesticides. Their production, import and usage were banned in the Czech Republic in 1974. It can be assumed that besides environmental contamination, chlorinated persistent pesticides, named in the Stockholm Convention (2001) as persistent organic pollutants (POPs) may be present in existing waste. That is why the proposal of the national plan for hazardous waste treatment considers the past and present methods of dealing with waste, and takes the prospect of this activity into account in the proposal for the national plan for dealing with hazardous waste in the Czech Republic.

CONCLUSIONS

Currently it is not easy to retroactively conduct an inventory of organochlorinated POP pesticides. The necessary amount of data regarding production, use, distribution and storage is not available or difficult to obtain and retrogressive reconstruction in some cases only leads to estimates. Despite this, it was possible to gain a basic overview of production, distribution and application of OCPs. Old obsolete stockpiles remain a problem which may be present locally, and which was not carefully liquidated in the past years. It is, among other things, also a consequence of the relevant legislation existing in the 1950s and 1960s which did not sufficiently identify exact rules for manipulation, storage and liquidation of unused stocks of these substances and preparations. A relatively good situation exists in the case of agricultural applications, where due to the existence of a former central registry, retrogressive reconstruction of the situation is possible, although some aspects are problematic. The situation is worse in terms of access to information about applications in communal hygiene or forestry.

Organochlorinated pesticides are not currently produced in the Czech Republic; there is no import and export either. The majority of stockpiles were liquidated in the first half of the 1990s. Due to their long-term production, and application, all POP pesticides are still detectable in abiotic and biotic environmental components, including humans.

There is also evidence of currently existing illegal deposits (dumping sites, stocks etc.), which is supported by discoveries, as well as for example increased levels of contaminants in the environment after floods.

ACKNOWLEDGEMENTS

The research reported here was supported by GEF/UNIDO, Project GF/CEH/01/003, Ministry of the Agriculture, CR, Ministry of Education, Youth and Sport (Project MSM0021622412 INCHEMBIOL) and RECETOX-TOCOEN & Associates.

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ORGANOCHLORINATED PESTICIDES (OCPS) IN THE CZECH REPUBLIC

PART II. OCCURRENCE AND LEVELS IN AIR, WATER AND SOIL

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OCCURRENCE OF OCPS IN AMBIENT AIR

Trends in the development of the medians of regional background concentrations of organochlorinated pesticides (DDTs, HCHs and HCB) are shown in Figures 1-3. These figures document the slightly decreasing tendency of monitored pollutants on a regional level but with respect to the local situation. Changes in the annual medians of OCPs reflect the results of floods in the CR (1997 and 2002).

OCCURRENCE OF OCPS IN THE HYDROSPHERE

The evaluation of the occurrence of POPs in selected layers of the hydrosphere and the formulation of the trends is not an easy matter. Although there is a consistent drop in the risk of POPs being emitted into the environment due to the termination of the production and use of these materials, production of new filters for sewage disposal and a larger emphasis on ecological policy in the country, the presence of POPs remains a significant ecological problem. In certain environmental issues some positive trends can be observed (i.e. a lower concentration in shallow waters), while in other cases related to the hydrosphere, these are more complicated to evaluate.

The impact of organochlorinated pesticides, for example DDT and its metabolites, polychloric cyclodienes (aldrin, endrin, dieldrin, isodrin) and isomers of HCH, on the hydrosphere is not particularly significant in the area of the Czech Republic and is comparable to that of other countries. However, there are regions with certain problems. In the case of DDT and its metabolites, Usti n/Labem and its chemical plant Spolchemie is an important source of this pollutant. Furthermore, another problematic area is in Neratovice with its plant Spolana, which can be demonstrated also by increased findings in the area Labe – Obříství. Higher levels of OCPs are observed in central and southern Moravia (for example: Dyje-Znojmo). In the case of HCH, the most severe situation is in central and southern Moravia, where the sediment particles found are in tens of ng.g⁻¹ and there are cases where they amount to hundreds of ng.g⁻¹. Moravian regions in comparison to Bohemian regions have higher amounts of polychlorinated cyclodienes, although in their case, the situation in absolute values does not seem to be too serious.
From the perspective of contamination by hexachlorobenzene in the Czech Republic, there is one very critical area, near the chemical plant Spolchemie in Usti n/ Labem. The release of HCBs from this plant into sewage water had and still has massive and negative impacts on all the components of the hydrosphere from the end of the riverbank of Bilina and Labe continuing to Germany. Significantly higher concentrations of HCB are measured here in comparison to other regions of the Czech Republic or other European countries; these are measured in the shallow waters of Bilina and Labe; and also in the sediment and suspended particles, aquatic biofilms and aquatic life. It is well known that the problem is being resolved on the factory side through technological modifications and more effective wastewater purification on the premises of the factory; however, it is important to continuously analyse the effects of lower HCB emissions in all components of the aquatic environment. Additional significant issues regarding the contamination of the hydrosphere by HCB in the Czech Republic are not currently known.

**OCCURRENCE OF OCPS IN SOIL**

Apart from systematic monitoring covered by the Central Institute for Supervising and Testing in Agriculture (CISTA), there exists a range of specific, short-term and targeted studies and experiments that can be of a monitoring character but that evaluate the particular state of contamination of the given soil during a given time period with reference to the sources of contamination and documenting a proposed arrangement. These studies use the results of systematic monitoring as a reference. Extensive monitoring of this type is provided by the Research Institute of Amelioration and Soil Conservation (RIASC). The activity of the Consortium RECETOX-TOCOEN & Associates is also presented regarding monitored POPs in soil.

**Monitoring CISTA (basal monitoring of soil)**

Until 1996 monitoring the content of organic pollutants was mainly done in terms of used pesticides and so each year the selected areas were those where wheat was harvested. Therefore the sample of the selected areas varied from year to year. From 1997, the content of the selected organic pollutants of the same area of estimated PP has been monitored in such a manner that the dynamics of the substances in the soil could be recorded even with regards to possible sources of long-distance transmission for some substances. A total of 40 sampling sites are being monitored, where 5 sampling sites are taken from the subsystem in protected areas on non-forest but undisturbed land (fixation of “background” values - an agreement with the Agency on Conservation of Nature in the Czech Republic). The remaining 35 sampling sites are selected from the monitoring of agricultural land, from both the basic subsystem and from the subsystem in contaminated areas. The selection is realised with regard to potential sources of contamination and on the previous observations in 1994-1996.

For four years (1994-1997) the organochlorinated pesticide contents were observed in a variable set of observational areas. In 1998 and 1999, these substances were not analysed in the soil. Now the results from the three previous years 2000, 2001 and 2002 are accessible where the samples were taken from a constant set of observational areas (35 observational areas from plough-land and 5 from the observational areas in conservation areas).

It is certain that the contents of these substances in agricultural soil remain high, but the question is the interpretation of the danger of its contents. The permissible level of pollution (10 ng.g⁻¹) set by notice 13/1994 is exceeded in around 13 % of the topsoil sample levels of HCB. In the case of DDT substances the situation is not that satisfactory, here the limit is exceeded in 73 % of the samples.

**CONCLUSIONS**

- In 2002, in comparison to previous years, there was a rise in HCB levels; the arithmetic mean for the topsoil range rose from 2.26 ng.g⁻¹ in 2000 to 7.34 ng.g⁻¹ in 2002 for the topsoil. A similar trend can be observed in the subsoil. However, the absolute values remain low.
- There has been a rise in the contents of the metabolites p,p'-DDE in the subsoil (median from 2.7 to 7.50 ng.g⁻¹ and arithmetic mean from 15.4 ng.g⁻¹ to 26.14 ng.g⁻¹ in 2002). For the metabolites o,p'-DDE; p,p' i o,p'-DDD, the contents have remained the same for the past three years.
- The annual comparison is applied to both the topsoil and subsoil thus the contents in the subsoil (arithmetic mean and median) are lower in 2000-2002.
- The limiting values as given in notice 13/1994 were exceeded mainly by measured levels of DDT in the years 2000 and 2001. In 2002 the limiting values as given in notice 13/1994 were exceeded in almost equal amounts by measured levels of both DDT (41) and DDE (40). In 2002 the exceeding limit was “only” in 18 samples and in DDE in 24 samples. In three years of observation, there was a decrease in exceeded limiting values in DDT (from 60 to 18) and there was an increase in DDE (from 14 in 2000 to 24 in 2002).
- In 2002, the limit as given in the notice on DDT and its metabolites was exceeded in 36.7 % of the samples.
- During the whole period of observation (1994-2002), there were significant fluctuations and therefore, unambiguous trends cannot be declared.

**MONITORING RIASC**

The monitoring of POPs in agricultural soil was initiated in 1993 by the Research Institute of Amelioration and Soil Conservation (RIASC) in the region of ecological strain of northern Bohemia. The whole concept of monitoring the state of strain in our agricultural POP soil is determined by the requirements:
- The soil of ecologically strained regions (north and west Bohemia and the northern Moravian region)
- The soil of regions under „regular strain“ in Bohemia and Moravia
- The soil surrounding the river Labe exposed to flooding.

From 1993 to 2001, monitoring was executed in 30 districts (from a total of 77), that are found in 6 regions (due to the current divisions of land). Samples of soil were taken from agricultural soil, and included in the monitoring pro-
gram were ploughing land, meadows and pastures. The goal was to achieve the most equidistant web of sample areas, where each one was around 25 km².

The concentration of HCB in agricultural soil is around 1.00 – 8.73 ng.g⁻¹ (geometrical means of concentrations, calculated for each district). In most of the monitored regions, the average concentration of HCB fluctuates between the found minimal concentrations; higher amounts were found in the districts of the northern Bohemia emission region, and the highest average value from the district of Ústí nad Labem. Here, the highest maximum value was detected (487 ng.g⁻¹); other distinctive values were found in the district of Litoměřice (337 ng.g⁻¹) and Sokolov (230 ng.g⁻¹).

The concentration of DDT in agricultural soil is around 1.00 – 5.62 ng.g⁻¹ (geometrical means of concentrations, calculated for each district). Those districts with a higher concentration of DDT are Kladno, Praha-West, Jičín, Benešov, and Karlovy Vary. In all other regions the average strain of DDT is around 3 ng.g⁻¹. The highest values were found in the district of Teplice (1 207 ng.g⁻¹), Ústí nad Labem (1 133 ng.g⁻¹), Prague-City (1 044 ng.g⁻¹), Karlovy Vary (398 ng.g⁻¹) and Jablonec nad Nisou (344 ng.g⁻¹).

DDT’s metabolites have a higher maximal average of concentration in DDE of around 1.00 – 9.62 ng.g⁻¹. The highest average value was found in Prague-West; those districts with a higher strain with a concentration greater than 5 ng.g⁻¹ are Kladno, Beroun, Příbram and Cheb. The highest maximum were found for Prague-City (1 054 ng.g⁻¹), Cheb (167 ng.g⁻¹), Jablonec nad Nisou and Jičín (159 ng.g⁻¹) and Teplice (146 ng.g⁻¹).

In the case of DDD the average concentrations appear lower, around 1.00 – 3.67 ng.g⁻¹. The highest average value is from the district of Benešov, while the surrounding district Kutná Hora was found to have the second highest average value of 2.48 ng.g⁻¹. In other monitored districts the average value of concentration is around 1 ng.g⁻¹. The highest maximum values were detected in the district of Teplice (256 ng.g⁻¹), Karvíná (49 ng.g⁻¹), Karlovy Vary (36 ng.g⁻¹) and Příbram (32.2 ng.g⁻¹).

For the purposes of some projects on the Labe, samples were taken from the flooded areas. There was a severe strain on the soil by not only risk elements but also by POPs. The chlorinated hydrocarbon content in the flooding samples was also significantly elevated. HCB exceeded the reference value in 41% of the taken samples. The flooded area has a relatively low amount of DDT and its metabolites. A mere 18 % of the samples exceeded the reference value for DDT and 12 % for DDE.

Despite terminating the usage of DDT, there continues to be an elevated level of its residuals in the whole territory of the Czech Republic, especially in the areas with intense agriculture.

**PROJECTS R-T&A CONCERNING SOIL CONTAMINATION**

The monitoring of POPs in the soil of the Czech Republic is also part of the TOCOEN project and its subprojects - TOCOEN/REGIONAL MONITORING (regional background monitoring in the Košetice observatory), TOCOEN/IDRIS (the soil in the Zlín area); TOCOEN/Mountains (soil and forest ecosystems in the mountain regions) and soil in the area of industrial sources (TOCOEN/Surroundings of model sources).

Regional background monitoring of POPs (POPs) is a part of the TOCOEN (Toxic Organic COMpounds in the ENVironment) project and it has been carried out in the area of the Košetice observatory since 1988. This monitoring is part of a long-term cooperation between the Czech Hydro-meteorological Institute and RECETOX - TOCOEN & Associates. The project TOCOEN is a long-term environmental research project that includes a number of Czech and foreign universities and institutions.

This part of the TOCOEN project is focused on the monitoring of polycyclic aromatic hydrocarbons (PAHs), organochlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs). Soil samples are taken annually from 9 locations characterizing different types (agriculture, meadow, forest) in the area of the observatory from 1988. At two selected locations PCDDs/Fs in soils are also monitored.

The TOCOEN/Mountains project is focused on the study of contaminated mountain spruce ecosystems. During the monitoring, the basic goal is to study the long-distance transport of these substances (the POP content present in the soil, needles and partially in the air) above the area of the Czech Republic and the secondary reaction to forest soil and the study of their presence in these ecosystems.

**Table 2. The concentration of organo-chlorinated pesticides in selected locations of the Czech Republic [ng.g⁻¹]**

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>Mountain, forest soil</th>
<th>Soil from the area of the Košetice observatory</th>
<th>Soil from industrial areas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptachlor epoxide A</td>
<td>BDL</td>
<td>2.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Heptachlor epoxide B</td>
<td>0.12 – 0.72</td>
<td>0.20 – 0.35</td>
<td>0.04 – 0.11</td>
</tr>
<tr>
<td>α-Chlordane</td>
<td>0.09 – 0.62</td>
<td>0.15 – 0.29</td>
<td>0.04 – 0.05</td>
</tr>
<tr>
<td>γ-Chlordane</td>
<td>0.06 – 0.48</td>
<td>0.09 – 0.25</td>
<td></td>
</tr>
<tr>
<td>Dieldrin</td>
<td>0.58 – 2.78</td>
<td>0.65 – 1.60</td>
<td></td>
</tr>
<tr>
<td>Endrin</td>
<td>0.00 – 1.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mel掬oxychlor</td>
<td>0.17 – 0.79</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Mirex</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3. The POP content in soil (median, minimum, maximum) from monitoring and research activities of Consortium R-T&A (HCHs, DDTs, HCB [ng.g⁻¹])**

<table>
<thead>
<tr>
<th>Area</th>
<th>ICHs (4 isomers)</th>
<th>DDTs (DDT + DDE + DDDD)</th>
<th>HCB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Košetice</td>
<td>0.59 (0.02 – 0.182)</td>
<td>3.6 (0.20 – 0.294)</td>
<td>0.55 (0.04 – 0.18)</td>
</tr>
<tr>
<td>Zlín</td>
<td>0.89 (0.02 – 0.51)</td>
<td>9.59 (0.72 – 1.018)</td>
<td>1.28 (0.02 – 0.25)</td>
</tr>
<tr>
<td>Beroun</td>
<td>1.03 (0.34 – 1.26)</td>
<td>8.8 (2.19 – 2.16)</td>
<td>2.54 (0.54 – 10.295)</td>
</tr>
<tr>
<td>Mokrá</td>
<td>0.74 (0.11 – 0.64)</td>
<td>14.45 (0.80 – 1.120)</td>
<td>0.75 (0.06 – 0.39)</td>
</tr>
<tr>
<td>High mountain ecosystems</td>
<td>1.34 (0.22 – 0.57)</td>
<td>55.0 (6.08 – 9.08)</td>
<td>2.21 (0.47 – 11.9)</td>
</tr>
<tr>
<td>Freeway</td>
<td>1.18 (0.17 – 1.46)</td>
<td>12.88 (0.43 – 35.56)</td>
<td>0.92 (0.05 – 0.6)</td>
</tr>
<tr>
<td></td>
<td>n = 45</td>
<td>n = 15</td>
<td>n = 21</td>
</tr>
</tbody>
</table>
One of the basic elements of the long-term strategy of the TOCOEN project is the monitoring of POPs in areas of selected industrial sources or in industrial regions with a high concentration of corporations and industry (Project TOCOEN/Surroundings of model sources); the soil is a basic component of the environment that is used for this purpose.

In the case of the national POP inventory, the laboratory RECETOX MU analysed the soil samples from the selected areas of the Czech Republic for the monitoring of other POP pesticides as stated in the Stockholm Convention (toxaphene, driens). Even in the case of these substances, it is possible to observe the higher amounts in mountain locations due to the long-distance transport, the sheeting effect in the forest and the accumulation of forest soil with a high content of organic carbon. The values for the toxaphene findings are shown in Table 1 below and for other types of pesticides (methoxychlor, chlordan, aldrin, dieldrin, mirex) in Tables 2 and 3 and in Figures 1 (overview of the sample locations) and 2.

The observed pesticides have not been used for over 20 years. However, it is possible to detect them in a number of locations, especially in mountain ecosystems as a product of long-distance transport.

The results from the above-mentioned projects and studies are stored in the archive of the TOCOEN project, and are partially available at: http://recetox.chemi.muni.cz/

The results of the long-term measurements of Consortium R - T & A are regularly published and confirm the measurement trends of CISTA and RIAS - a higher contamination in higher geographical locations due to long-

### Table 7. Values of toxaphene found in the soil from a variety of locations in the Czech Republic

<table>
<thead>
<tr>
<th>Location</th>
<th>Period of sampling</th>
<th>Type of sample</th>
<th>Sum of 22 TOX [ng.g⁻¹]</th>
<th>Sum techn. toxaphen [ng.g⁻¹]</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Southern Moravia, Velká Bítěš</td>
<td>2003</td>
<td>Forest soil</td>
<td>1,3</td>
<td>9,1</td>
<td>In lower areas toxaphene was monitored only in the matrices with a high content of Cₐₑ₉ (~20 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Agricultural soil</td>
<td>&lt; 0,1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Plant litter</td>
<td>1,1</td>
<td>4,9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pine needles</td>
<td>&lt; 0,6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Southern Bohemia, Košetice</td>
<td>2001</td>
<td>Forest soil</td>
<td>1,9 - 2,3</td>
<td>9,9 - 12,2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Agricultural soil</td>
<td>&lt; 0,1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Plant litter</td>
<td>5,4</td>
<td>14,5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pine needles</td>
<td>&lt; 0,6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coastal Mountain</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Krkonoš, Alžbětiny</td>
<td>2001</td>
<td>Forest soil</td>
<td>9,0</td>
<td>51,4</td>
<td>The locations with a higher altitude, the highest values under LOD in soil with Cₐₑ₉ &lt; 5 %</td>
</tr>
<tr>
<td>Krkonoš, Pudlova</td>
<td></td>
<td></td>
<td>7,3</td>
<td>49,4</td>
<td></td>
</tr>
<tr>
<td>Krkonoš, Modrý důl</td>
<td></td>
<td></td>
<td>9,5</td>
<td>56,9</td>
<td></td>
</tr>
<tr>
<td>Krkonoš, Pašeráký chodníček</td>
<td></td>
<td></td>
<td>7,9</td>
<td>46,0</td>
<td></td>
</tr>
<tr>
<td>Šumava Boublín</td>
<td></td>
<td></td>
<td>4,5</td>
<td>25,0</td>
<td></td>
</tr>
<tr>
<td>Krušně Mountains, Našťín</td>
<td></td>
<td></td>
<td>9,0</td>
<td>60,7</td>
<td></td>
</tr>
<tr>
<td>Krušně Mountains, Červená jáma</td>
<td></td>
<td></td>
<td>3,2</td>
<td>28,2</td>
<td></td>
</tr>
<tr>
<td>Lužické Mountains, Jedlová</td>
<td></td>
<td></td>
<td>3,0</td>
<td>27,2</td>
<td></td>
</tr>
<tr>
<td>Jeseníky, Červenohorské sedlo</td>
<td></td>
<td></td>
<td>3,4</td>
<td>19,9</td>
<td></td>
</tr>
<tr>
<td>Jeseníky, Červenohorské sedlo (litter)</td>
<td></td>
<td></td>
<td>3,4</td>
<td>13,2</td>
<td></td>
</tr>
<tr>
<td>Beskydy, Bílý kříž</td>
<td></td>
<td></td>
<td>1,4</td>
<td>12,4</td>
<td></td>
</tr>
<tr>
<td>Bílé Karpaty, Pláňava</td>
<td></td>
<td></td>
<td>&lt; 0,1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 locations of the basal monitoring of soil, CISTA</td>
<td>2001</td>
<td>Agricultural soil, meadows</td>
<td>&lt; 0,1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
distance transfer and the accumulating properties of mountain forest ecosystems and presently also a decreasing trend of concentrations of OCPs within the past decade. An overview of long-term results is shown in Table 3.

ACKNOWLEDGEMENTS

The research reported here was supported by GEF/UNIDO, Project GF/CEH/01/003, Ministry of the Agriculture, CR, Ministry of Education, Youth and Sport (Project MSM0021622412 INCHEMBIOL) and RECETOX-TOCOEN & Associates.

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

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ABSTRACT

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

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

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

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

915 tons of stocks of obsolete pesticides have been discovered so far during the inventory over the five regions in the Russian Federation (Archangelsk, Magadan, Omsk and Tyumen regions, Republic of Komi). 233 tons of unidentified pesticides have been analyzed, and 93 tons repackaged in three regions. In addition to the contributions of the Arctic Council countries, Russian local authorities have contributed substantial funds from their local budgets. KEYWORDS: OBSOLETE PESTICIDES, ARCTIC COUNCIL, ACAP, RUSSIA.

FRAMEWORK FOR ACTION

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

INVENTORY AND SAFE STORAGE OF STOCKS OF OBSOLETE PESTICIDES IN THE RUSSIAN FEDERATION

Reducing releases of obsolete pesticides from legacy stocks is the objective of several international projects throughout the world. The Arctic Council Action Plan to Eliminate Pollution of the Arctic (ACAP) has been carrying out such a project in the Northern territories of the Russian Federation since 2001. The project was developed as a response to the environmental information presented by the Arctic Monitoring and Assessment Program (AMAP) of the Arctic Council. The major Russian river systems flow north, with the exception of the Volga River, contributing significant amounts of pesticides into the Arctic Basin (see Figure 1).

This project is carried out under the Arctic Council Action Plan (ACAP) with the participation of the Russian Federation, Canada, Denmark, Finland, the Netherlands, Norway, Sweden, and the USA.

REFERENCE

Russia has a large stock of obsolete and prohibited pesticides estimated at more than 24,000 tons. The existing data, prior to this project, indicated the presence of 3000 tons of obsolete pesticides in the northern regions. As the data were based on existing documentation only, it was expected that the comprehensive inventories based on actual warehouse investigations would provide higher results. This was demonstrated by the identification of an additional 800 tons in five priority regions. In addition, the existing information contained only agricultural pesticides, and this ACAP Project obtained information on other stockpiles, such as veterinary, forestry, and sanitary pesticides.

At preparatory phase of the Project, ACAP identified 11 Russian priority regions that directly impact the Arctic. These priority regions include Archangelsk (including the Nenets Autonomous District), Komi, Krasnoyarsk Krai (including the Taymyr Autonomous District), Magadan (including the Chukchi Autonomous District), and Murmansk. Sub-arctic regions include Altai Krai (including the Altai Republic), Kurgan and Omsk. The Arctic River Basin is shown in Figure 1.

SOURCES

The reasons for the accumulation of obsolete pesticides in the Northern Russian territories are as follows:

• Pesticides stored too long, i.e., exceeding their shelf-life,
• Changes in product registration and approval,
• Excess quantities provided by off-farm authorities (Soviet legacy pesticides),
• Leftovers from donations under international development assistance programs,
• Damage or loss of identity due to poor storage conditions.

ENVIRONMENTAL CONCENTRATIONS

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

ENVIRONMENTALLY SOUND MANAGEMENT OF STOCKS OF OBSOLETE PESTICIDES IN THE RUSSIAN FEDERATION

This ACAP project was initiated to collect inventory information and ensure environmentally sound management of obsolete pesticides stockpiles in Northern Russia to remove the threat to public health and the environment. The project consists of three phases:

Phase I – Development of inventories in eleven selected priority regions of the Russian Federation, to include screening analysis for the presence of mercury, arsenic and chlorinated organics.

Phase II

• Improvement of temporary storage conditions, including repackaging and labelling, and consolidation of stocks of waste pesticides. It was decided that none of these pesticides would be considered for reuse.
• Assessment and selection of the best available technologies and methods for destruction/disposal of pesticides stocks.

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

MODEL INVENTORY, ANALYSIS, AND REPACKAGING

Archangelsk was selected as the first region for a complete inventory, screening analysis, collection, repackaging, and the temporary storage of stocks of obsolete pesticides. Archangelsk is located at the Arctic Circle on the White Sea in Northwest Russia.

Stocks of obsolete pesticides in the Archangelsk region had already been identified as an environmental “hotspot” by the Barents Euro-Arctic Council.

The Archangelsk Plant Protection Station took the lead in the development and implementation of this model project. The analytical laboratory of Archangelsk Sanepidnadzor performed a screening analysis. Coordination of the project between the Russian performing entities and the donor countries was carried out by the Center for International Projects in Moscow. This project also received financial support from the Archangelsk Regional Administration.

The initial registered inventory, prior to the start of this ACAP Project, was 43,000 kg. The detailed inventory performed under this ACAP project in 2003-2004 resulted in a fifty percent higher inventory of obsolete pesticides (62,752 kg) in the region. Of these, 14,443 kg were unidentified preparations and mixtures, which were sampled and analyzed for disposal. 57,046 kg of obsolete stocks were repackaged, and 109 storage facilities were evaluated and their
conditions documented. Some of the unsafe storage facilities were dismantled. The repackaged pesticides were transported to environmentally safe warehouses. These pesticides have been effectively isolated from release into the Arctic environment.

It was mutually decided that under this ACAP Project no obsolete and prohibited pesticides will be discarded by dumping into landfills.

The results of this model demonstration project were presented at the parliamentary hearings of the Russian Duma in April 2004, and received a strong endorsement there.

Using the model and experience in Archangelsk, an inventory, screening analysis, collection and repackaging program has now been completed in Komi and Magadan. Work in the Altay Republic, Kurgan, Tyumen, and Omsk Regions is currently in progress. The amount of obsolete pesticides in these regions has turned out to be considerably higher than suggested by the data prior to the inventories. By March 2005, more than 800 tons of obsolete pesticides were inventoried. The majority of the pesticides have also been repackaged. Stocks were analyzed for heavy metals (and chlorinated compounds).

**PRACTICAL LESSONS**

- The implementation of the activities requires the effort of all relevant agricultural, forestry, sanitary and veterinary agencies and experts.
- It is useful for the project steering committee to meet and work directly with the regional experts to receive the best possible information for the funding decisions and project development.

<table>
<thead>
<tr>
<th></th>
<th>Estimated stocks before project (tons)</th>
<th>Known stocks after detailed inventories (tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Archangelsk</td>
<td>41</td>
<td>62</td>
</tr>
<tr>
<td>Komi Republic</td>
<td>14</td>
<td>19</td>
</tr>
<tr>
<td>Magadan</td>
<td>16</td>
<td>23</td>
</tr>
<tr>
<td>Tyumen</td>
<td>40</td>
<td>233</td>
</tr>
<tr>
<td>Omsk</td>
<td>464</td>
<td>578</td>
</tr>
<tr>
<td>Altay Republic</td>
<td>20 +</td>
<td>to be determined</td>
</tr>
<tr>
<td>Altay Krai</td>
<td>1414</td>
<td>to be determined</td>
</tr>
<tr>
<td>Kurgan</td>
<td>1025</td>
<td>to be determined</td>
</tr>
<tr>
<td>Krasnoyarsk Krai</td>
<td>38</td>
<td>to be determined</td>
</tr>
<tr>
<td>Republic of Sakha</td>
<td>30</td>
<td>to be determined</td>
</tr>
<tr>
<td>Kamchatka Region</td>
<td>9</td>
<td>to be determined</td>
</tr>
<tr>
<td>TOTAL</td>
<td>3111</td>
<td>To date 915</td>
</tr>
</tbody>
</table>

*Table. The detailed inventories revealed that the amount of obsolete pesticides is higher than expected*

**Before:** Obsolete and prohibited pesticides storage in Komi Republic 30 April 2004.

**After:** Old warehouses are often contaminated and must be cleaned. Komi Republic, late summer 2004.
• Due to long distances and the large number of warehouses, it is economically desirable to perform all the work (inventory development, assessment of storage facilities, sample collection, repackaging, and transportation to the safe warehouses) in one visit to a district.

• Weather is a significant constraint in doing this work; therefore advance planning is necessary to ensure completion of all work during the “weather window.”

CONCLUSIONS

This project is a prime example of actions by the Arctic nations to address the danger of stockpiles of obsolete pesticides in the Arctic.

The ultimate objective of the project is the environmentally sound destruction of these obsolete pesticides stockpiles to remove the threat to the public health and the environment.

As a result of the successful development and demonstration of this model approach in these Arctic regions, the Russian Federation has agreed to apply this model in other regions of Russia containing stocks of obsolete and prohibited pesticides.

To date, all stocks in Archangelsk (64 t), Magadan (20 t) and Komi (18 t) have been repackaged, analyzed and safely stored. Similar projects in Tyumen (233 t) and Omsk (578 t) will be completed in 2005. More than 915 tons of obsolete and prohibited pesticides were discovered during the inventory development in the first five regions. 233 tons of unidentified pesticides were analyzed and 93 tons repackaged. $95,000 was contributed by the Russian Regions to co-fund, together with donor countries, these ACAP Regional Projects.

Projects in the Altai Republic (Gorny Altai) and Kurgan, where pre-inventory data suggests 20 and 1025 tons of obsolete pesticides, have started. The Project in Altai Krai (1414 tons) is pending additional funding from donors and three priority regions remain for the completion of this project. The next phase of this project will be destruction of the obsolete pesticides.

ANALYSIS OF THE CURRENT STATUS OF TREATMENT OF PROHIBITED AND OBSOLETE PESTICIDES IN THE CONTEXT OF THE DEVELOPMENT OF THE NATIONAL PLAN FOR IMPLEMENTATION OF THE STOCKHOLM CONVENTION ON PERSISTENT ORGANIC POLLUTANTS

Ye. V. Ligostayeva

A.V. Antonov
Project Technical Expert

The legislation of Ukraine settles all basic issues related to treatment of pesticides and agrochemicals, including persistent organics pollutants (POP’s), in view of the international agreements, signed by, and also requirements of the Commission «Codecs Alimentarius».

Practically all pesticides which are included into list of POP’s to the Stockholm Convention and the Report about POP’s, are prohibited on the territory of Ukraine. Some of them are not included in „The list of the prohibited pesticides in agriculture which cannot be registered or re-registered in Ukraine“. They are not registered on the territory of Ukraine and under the Law of Ukraine « About prohibited and obsolete pesticides and agrochemicals» their import, production, sales, application and advertisement is prohibited.

The accumulation of prohibited and obsolete pesticides (OP) in Ukraine began in 1970 - 1980, after prohibition of some pesticides in agricultural production. It is necessary to note, that the Resolution of the Chief State Health Officer of the USSR on prohibition of application of these pesticides, did not include prohibition for their production and during the period from 1953 up to 1986 manufacture of DDT in a chemical plant in Kiev (enterprise “ Radical “) with up to 40 thousand tons per year continued.

The Resolution of the Council of Ministers of the USSR about concentration of the prohibited pesticides in special time warehouses, with their subsequent export to enterprises - manufacturers for processing and destruction was adopted to bring order to the process of treatment of prohibited pesticides.

In the process of implementation of this Resolution, the majority of pesticides in Ukraine had been taken out to the above-stated warehouses (“SELHOZCHEMICAL”), the remaining part stayed at the warehouses of agricultural productions, i.e. in places of their temporary storage. In most cases those were places that were not appropriate for long-term storage of hazardous substances.
Despite of development of the national legislation and regulation, (5 Laws of Ukraine and a number of legislative acts of different levels), the problem of the OP treatment was never addressed properly in Ukraine for more than 30 years.

It is necessary to note, that this problem is to large extent common and typical for the majority of former republics of the USSR. On Photo 1-3 the most typical illustrations describing conditions of places of storage of OP in Ukraine are presented; on Photo 4 - a typical condition at a warehouse of OP storage after carrying out a process of re-packaging within the framework of the Ukrainian - Danish project «Elimination of the risk related with accumulated or prohibited pesticides». Within the framework of implementation of this project, approximately 3000 tons of OP was re-packed in polymeric tanks, which created a most positive impact on the reduction of risks of occurrence of negative situation, related to the opportunity of OP leakage into ground water, soil, and also to their uncontrolled unauthorized use. There have been cases of occurrence of fires as a result of chemical self-ignition of OP because of violation of technology of re-packing process (Photo 5 and 6).

Within last three years regional departments of the Ministry of Agrarian policy, the Ministry of Environmental Protection and Ministry of Health of Ukraine carried out com-

![Photo 1. Typical kind inside a warehouse of the OP storage](image1)

![Photo 2. Typical situation inside a warehouse of the OP storage](image2)

![Photo 3. Typical kind inside a warehouse of the OP storage](image3)

![Photo 4. Typical kind inside a warehouse of the OP storage, re-packing within the framework of implementation of Ukrainian - Danish project](image4)

![Photo 5. Warehouse after fire as a result of chemical self-ignitions of the OP, packing done with violation of technological process](image5)

![Photo 6. Appearance of a warehouse with OP after fire](image6)
plex inventory of places of accumulation and of quantities of OP. One task of the Project GEF/UNEP “Enabling Activities for the development of the National plan for implementation of the Stockholm Convention on POP’s in Ukraine” was specification, and actualization of the inventory data on POP’s. Taking into account the data received as a result of implementation of the Ukrainian - Danish projects in sphere of treatment of pesticides and the state specified complex inventory, the format of the proper inventory register was developed. This register includes data on sites and forms of ownership of warehouses, ranges, burial grounds, etc. where pesticides, including POP’s, are placed and displayed, their amount (including unidentified), conditions of storage, data on integrated estimation of risk and actions carried out with the purpose of prevention of negative impact on environment and health of people.

In Table 1 the generalized data of preliminary inventory of the prohibited and obsolete pesticides, including POP’s, in a separate region - the Kiev area are presented, and in Table 2 includes data on Ukraine as a whole, including detected industrial wastes - POP’s.

Only in Kiev area 1932.86 tons of pesticides were detected and brought in the inventory register of places and conditions of storage of the prohibited and obsolete pesticides, including POP’s, in a separate region - the Kiev area are presented, and in Table 2 includes data on Ukraine as a whole, including detected industrial wastes - POP’s.

In view of repeated re-packing, changes of owners, losses of marks, the data on amount and type of prohibited and obsolete pesticides (including those containing POP’s) are approximate and require constant actualization. In view of non-economical, and often impossible differentiation of POP’s and majority of OP at their storage sites (about 5000), the amount of POP’s should be counted as the sum of detected identified POP’s and unidentified OP. Thus, as of 1st quarter of 2005, the amount of the substances accumulated in Ukraine falling under the requirements of the POP’s, comes nearer to the amount of approximately 30000 tons.

Differentiation of the detected places of storage and amount of the prohibited and obsolete pesticides, and also industrial wastes - POP’s on regions of Ukraine is presented on Images 1-3.

<table>
<thead>
<tr>
<th>Detected and included into register of the prohibited and obsolete pesticides including POP’s</th>
<th>Detected and included in the register of a place of storage of pesticides (quantity)</th>
<th>Condition of warehouses and containers</th>
<th>Containered tons</th>
<th>Quantity of containers</th>
<th>It is destroyed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>DDT</td>
<td>HCH</td>
<td>Not identified</td>
<td>Satisfactory</td>
<td>Un satisfactory</td>
</tr>
<tr>
<td>quant.</td>
<td>%</td>
<td>quant.</td>
<td>%</td>
<td>quant.</td>
<td>%</td>
</tr>
<tr>
<td>1932.86</td>
<td>265</td>
<td>2.42</td>
<td>1665.44</td>
<td>262</td>
<td>178</td>
</tr>
</tbody>
</table>

Table 1. The generalised data on inventories of places and conditions of storage of the prohibited and obsolete pesticides, including POP’s in Kiev region

burial ground – at a temporary storage near with Altestovo village:
• HCH, lindane – 273.1 tons;
• heptachlor – 1.4 tons.

In view of repeated re-packing, changes of owners, losses of marks, the data on amount and type of prohibited and obsolete pesticides (including those containing POP’s) are approximate and require constant actualization. In view of non-economical, and often impossible differentiation of POP’s and majorit of OP at their storage sites (about 5000), the amount of POP’s should be counted as the sum of detected identified POP’s and unidentified OP. Thus, as of 1st quarter of 2005, the amount of the substances accumulated in Ukraine falling under the requirements of the POP’s, comes nearer to the amount of approximately 30000 tons.

Differentiation of the detected places of storage and amount of the prohibited and obsolete pesticides, and also industrial wastes - POP’s on regions of Ukraine is presented on Images 1-3.
The biggest concentration of DDT can be found in the Odessa, Zaporozhye, Kiev, Volynsk and Poltava regions. Analysis of results of supervision over pollution of soils with persistent organic pollutants in 1994-2003 demonstrated that regions of Ukraine substantially differ in terms of POP’s pollution. During the last 10 years, agricultural soil pollution by POP’s was almost systematically observed in Zaporozhye, Vinnitsa, Kherson and Donetsk areas. In separate regions of Ukraine the non-authorized utilization of chlororganic pesticide DDT on agricultural lands is observed, especially in gardens and vineyards.

As a whole, the tendency of POP’s pollution of investigated rivers has essentially decreased in comparison with the earliest period. According to the data available from literature, during the period from 1979 for 1985 in the mouth of Dnepr river maintenance of DDT fluctuated in the range from 0,1-0,6 mkI / dm³. The data from literature on the quantity of DDT in the mouth of Dnepr river for later periods could not be detected.

Analysis of the current status of treatment of prohibited and obsolete pesticides in the context of the development of the National Plan for Implementation (NIP) of the Stockholm Convention on Persistent Organic Pollutants, taking into consideration all the abovementioned, allows the design of the following draft of the list of National priorities in this area:

• mobilization of resources and covering expenses, including foreign investments to the implementation of the NIP of the Stockholm Convention on POP’s in Ukraine. Creating appropriate conditions for attracting foreign investment for the execution of separate projects.

• development of the national legislative base regulating the POP’s management, according to requirements of the Stockholm Convention on POP’s and other international documents.

• selection of the most appropriate technology from ecological and economic point of view for POP’s disposal as well as polluted objects and territories. At an initial stage, 5-6 pilot projects for POP’s disposal in separate areas (Lvov, Kiev, Vinnitsa, Odessa, AR Crimea, etc.) should be conducted. This experience should be extrapolated to other regions.

• disposal (reprocessing) of accumulated stocks (more than 11000 tons) HCB - a production waste of the four-chloride carbon stored on range of toxic waste products of “Oriana-Galev” LTD. Kalush, Ivano-Frankovsk areas, closing this production facility, monitoring of the specified site.

• disposal (decontamination) of the prohibited and obsolete pesticides - POP’s with application of modern ecologically safe technologies.

• detecting POP’s polluted soils and territories, their remediation with utilization of modern, including agro- and biotechnologies.

• development of analytical base and improvement of system of POP’s monitoring, carrying out of research works to deal with problems of the POP’s treatment;

• carrying out active information policy among the public and the interested parties on issues of the POP’s treatment.

The international obligations of Ukraine related with the Stockholm Convention on POP’s and fulfillment of its provisions, have multilateral and long-term character and require appropriate funding. At the same time they provide the combined approach, namely:

• involvement of the separate national economic mechanisms to support the implementation of actions according to the requirements of Convention (within the framework of opportunities of the country);

• consolidations of financial opportunities of the country and of enterprises (corporations);

• granting various international technical assistance and financial resources on a multilateral or bilateral basis.

Implementation of the National actions necessary for the achievement of goals of the Stockholm Convention regarding resolution of the problem of treatment of the prohibited and obsolete pesticides, and also industrial wastes - POP’s, according to approximate calculations of national and international experts demands allocation for the period of 2005-2028 of the total funding amount of 110-130 million $.
PESTICIDES IN KAZAKHSTAN

Lidiya Astanina


Accumulation of large quantities of banned, unwanted and obsolete pesticides is a serious problem for agricultural sector of the Republic of Kazakhstan.

Large quantities of unaccounted pesticides are stored in the country. Imported and unused in 60-80-ies pesticides are stored in unadapted, shabby premises, often with leaking roofs, dumped in a heap. Underground waters carry these pesticides into rivers and other water bodies causing significant damage to the environment.

Considerable amounts of pesticides are found on the areas of completely destroyed storehouses, which are not mentioned in the official materials.

Sanitary-epidemiological units of Kazakhstan’s Health Protection Agency conduct monitoring of health support environments which can contain some data sets related to pesticides subject to utilization and conservation. These data sets suggest that despite 5-6 times decrease in pesticides burden on soils, the overall pesticides pollution problem remains quite acute. Higher than nationwide average residual pesticides pollution levels are identified in the Kostanai, South-Kazakhstan and Western-Kazakhstan regions, where preliminary estimates indicate that stocks of pesticides are not particularly large.

Kazakhstan mainly imports pesticides. “KZ”, the only pesticide produced in Kazakhstan (Pesticide Ltd., Shymkent) is not a POP.

Key foreign suppliers dealing with local companies include Ufachemprom (Russia), Zeneca (United Kingdom), Uniroyal Chemical (USA), Novartis (Switzerland), Rhône Poulenc (France), Monsanto (USA). Volumewise 2.4 D-aminic salt imported from Russia is the leader in pesticides shipments to Kazakhstan.

However, considering that Kazakhstan has transparent borders with Russia, Uzbekistan and Kyrgyzstan it is conceivable that in addition to registered Kazakhstani pesticides importers there are also companies illegally shipping pesticides to Kazakhstan including persistent organic pollutants. For example, a number of openly sold chemical household items include DDT and GCCG components and were smuggled to Kazakhstan.

In the beginning of 2004 a preliminary inventory of obsolete and unwanted pesticides was completed. It was undertaken within the UNDP/GEF Project «Initial Assistance to the Republic of Kazakhstan to Meet its Obligations under the Stockholm Convention on POPs». The goal of the inventory was identification of old abandoned, unregistered, destroyed pesticide storage sites; identification of POPs compounds among stored pesticides and their mixtures; quantification of unwanted pesticides and their packages.

This work is not as that simple as it could seem at first sight. Pesticides are often stored as mixtures requiring identification (through expensive physical and chemical analysis techniques). The storage sites themselves are sometimes difficult to find considering their destroyed and abandoned state.

The total amount of pesticides and their mixtures found during the inventory of “Selkhozkhimiya” former storage sites, former kolkhozs and sovkhozs storage sites and agricultural aviation airfields is 1500 tons. Additionally the estimation of obsolete pesticides buried in closed and functioning burial grounds has yet to be made. Finally, they all will have to be extracted from the burial grounds and disposed of in accordance with the requirements of the Stockholm Convention on POPs.

The fulfilled work is the first after the USSR break up but still only a preliminary inventory of pesticides in local storage sites, - report of the results of the preliminary inventory of obsolete pesticides in Kazakhstan contains this information.

Within the undertaken inventory of obsolete pesticides 140 storage sites have been inspected; only 57 are functioning – 83 former storehouses of «Selkhozkhimiya» are completely destroyed. Mixtures of pesticides with soil or mineral fertilizers are often found on their areas. On average, the share of unidentified pesticides mixtures is 72% of the total amount of found pesticides. It could be presumed that these mixtures may also contain POPs pesticides.

Apart from pesticides the issue of package disposal has also to be addressed. According to the preliminary data of the national inventory the number of packages to be disposed of exceeds 300 thousand. The packages can be dangerous for human health since they are widely used for household purposes (food and water storage). The population knows little of this danger.

The main reasons leading to accumulation of obsolete pesticides are: ban of purchased compounds due to high toxicological or environmental hazards; fall of demand for pesticides due to their low efficiency, low storage stability and high fire risk; damaged packages; expiration of application time.

In connection with large amounts of obsolete pesticides stored in Kazakhstan, the issue of their treatment with further disposal is highly topical. The inventory showed the importance of designing, construction and maintenance of burial grounds for toxic wastes. Currently, Kazakhstan has only two functioning burial grounds (in Kustanai and Pavlodar oblasts).

It is important to search for pesticides storage facilities owned by private entrepreneurs and assess conditions of these facilities (currently owners of such storage facilities are not registered, access to facilities is limited, while external observations indicate unsatisfactory state of the facilities. Also, in Kazakhstan there are abandoned pesticides warehouses).

The preliminary inventory of obsolete pesticides within UNDP/GEF Project allowed identifying a number of problems in agricultural chemicals management. They are listed below:

– Lack of framework for obsolete pesticide management and lack of a state body responsible for this management.
INTENSIVE APPLICATION OF CHEMICALS – RESULTS ARE HARD TO UNDERSTATE

Olga Speranskaya

More than 30% of pesticides in the former USSR were produced in excess of reasonable economic or production needs. In the USSR, pesticides were assumed as a vital necessity and as an inevitable factor of agriculture production. Distribution of pesticides among different regions was made without any accounting for local environment and climate conditions, nothing to say about accounting for rates of their environmental detoxification.

Besides that, in the majority of cases, pesticides were stored in unsuitable storage facilities. At the same time, authorities withheld information on serious adverse health and environmental impacts of pesticides. Immediate positive effects of pesticide application obscured less evident long-term adverse environmental impacts of application of these chemicals - i.e. the fact that a newly cleared environmental niche may be immediately occupied by a new, potentially more dangerous population. Even more serious adverse effects of faceless application of pesticides were associated with migration of toxic substances in environmental media and accumulation of their toxic residues in drinking water, wild and agricultural plants, in food products of plant and animal origin.

50 years of intensive application of pesticides in many regions of Russia resulted in serious environmental changes, including some irreversible ones. It is well known, that not withstanding the imposition of the absolute ban on DDT use, since 1972, its application was merely limited but not prohibited. The large scale application of chemicals in agriculture resulted in thousands of abandoned or dilapidated storage facilities (in the majority of cases, these facilities are located nearby water bodies). After the recent decline of agricultural infrastructure, many storage facilities (as well as residual pesticides) became abandoned. In many cases, abandoned pesticides and fertilisers may be found nearby roads, in forests, ravines, nearby water bodies, etc. So far, Russia has failed to complete a full inventory of obsolete, banned and unusable pesticides and their storage facilities at the national territory.

As a result of preliminary inventories (based on official sources of information) the following facts were revealed. As at early 2003, more than 24 thousand tons of obsolete pesticides were identified, many of these chemicals belong to highly toxic persistent substances and their storage conditions do not meet applicable requirements. The most high amounts of obsolete pesticides were identified in Krasnodar Krai (2.7 thousand tons), in Rostov Oblast, Voronezh Oblast, Kurgan Oblast, Altai Krai (about 1.0 thousand tons in each region). The largest stockpiles of such pesticides were accumulated in the Southern Federal District (more than 4.6 thousand tons). In 1997, the framework law of Russia in the sphere of pesticide management was approved - Law on Safe Management of Pesticides and Agrochemicals. The Law stipulated the division of responsibilities and measures of state control in the course of registration, transportation, application of pesticides, storage and utilisation of unusable chemicals. However, from that time, the situation in the sphere of management of obsolete and unusable pesticide did not improve.

It is clear that it would be impossible to conduct a complete inventory of these chemicals without mobilisation of all social sectors. Therefore, it is very important to develop methodologies for primary inventory of obsolete, unusable and banned pesticides and agrochemicals, to discuss these methodologies with representatives of interested non-governmental organisations. Such methodological recommendations have been prepared by Eco-Accord in cooperation with The Committee on Environment of the Russian Parliament. This material serves as a tool for local communities, non-governmental organisations, all parties, interested in identification of illegal storages of these hazardous chemicals. Practical application of the recommendations should be accessible to the general public and should become a component of official reports on inventory of obsolete pesticides.
THE STATE OF OBSOLETE PESTICIDES IN BOSNIA & HERZEGOVINA

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INTRODUCTION
In Bosnia and Herzegovina there is no the pesticides production of any kind.

The consumption of pesticides, belonging to all groups, according to the target organisms up to the war (1992) was 2500 tons annually. There is no an accurate data regarding the consumption of POPs pesticides, for the period when its application was allowed. However, the pesticides application has not always been in correspondence with the “Good agricultural practice”.

The Integrated Pest Management (IPM) is being implemented only to a small degree because of lack the Professional Plant Protection Services.

In most cases the pesticides are being purchased through agricultural pharmacies, for small farmers, and through wholesale dealers for big enterprises.

PRODUCTIONS, DISTRIBUTION, USE, EXPORT, IMPORT PROCEDURES OF POPS
In the period from 1992 to 1995, the pesticides were used in very small quantities, but some of POPs pesticides an obsolete push were (DDT, HCH, DNOC) and imported from Serbia and Montenegro.

All groups of pesticides are imported, but those obsolete ones that are in use are being imported illegally. The PIC Procedure will be in use probably in 2006.

The residua of some active pesticides components in the soil, according to the professional and research data, are recorded to be above the tolerable level.

The residue of DDT and HCH pesticides in the surface waters in the area of Sarajevo, has been recorded (Numic, 2001) following the research. The level of the residue of the majority of pesticides in food and feed is within the tolerance level. The current legislation related to obsolete POPs-Pesticides in B&H is presented in the following table:

<table>
<thead>
<tr>
<th>Name</th>
<th>Current regulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDT</td>
<td>Consumption is banned</td>
</tr>
<tr>
<td>Aldrin</td>
<td>Consumption is banned</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>Consumption is banned</td>
</tr>
<tr>
<td>Chlorodane</td>
<td>Consumption is banned</td>
</tr>
<tr>
<td>Endrin</td>
<td>Consumption is banned</td>
</tr>
<tr>
<td>Haptachlor</td>
<td>Consumption is banned</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>Consumption is banned</td>
</tr>
<tr>
<td>Mirex</td>
<td>Consumption is banned</td>
</tr>
<tr>
<td>Toxaphene</td>
<td>Consumption is banned</td>
</tr>
</tbody>
</table>

Methyl Bromide is under phase-out (2006).

Although the investigation of pesticide residue in the fatty tissue of humans has been performed in a very small number of patients, the presence of DDT and HCH was detected in quantities above the tolerance.

Stocks of POPs pesticides: It is possible that the POPs pesticides, in certain quantities, are stored near the site of agricultural pharmacies and veterinary stations. Contaminated sites of POPs pesticides are soil (arable, forests, uncultured), water (subsurface, ground, underground, lakes) and the fatty tissue of humans and animals. It is also possible that some food and feed are contaminated.

Pesticides of all type formulation have been wasted by the filling the land. Also the containers for the pesticides after the application are being stored-wasted in the soil. Incineration is not so often used for the pesticides chemical decomposition. Alternative technologies have not been utilized. Monitoring of POPs pesticides is not obligatory but has been done occasionally.

Legislation in Bosnia and Herzegovina by the Low Lex Specials of the regulation of pesticides being covered by the following lows:


In the Federation of Bosnia and Herzegovina the lows dealing with the pesticides are:

In Republika Srpska the lows dealing with the pesticides are:


The environmental protection legislation in Bosnia and Herzegovina also dealing with the pesticides is the following:

Adopted by the Entity (date of adoption):

- Low on Environmental Protection 19 July 2003 24 August 2002
- Low on Nature Protection 19 July 2003 24 August 2002
- Low on Waste Management 19 July 200 24 August 2002
- Low on Air Protection 19 July 2003 24 August 2002
- Low on Waters Protection 19 July 2003 24 August 2002

Low on Fund for Environment Protection in the Federation of Bosnia and Herzegovina does not exist.

The sub legislative dealing with the pesticides is as follows:


Institutions dealing with pesticides are: Faculty of Agriculture, University of Sarajevo, Institute of Human Health, Sarajevo. The POPs pesticides have been investigated before 1992, at the Faculty of Medicine, Faculty of Pharmacy and Faculty of Agriculture of the Sarajevo University. After the war, studied has been performed at the Faculty of Agriculture University of Sarajevo.

Human health assessments: the influence of POPs pesticides on human health has been occasionally studied. However, there is no systematic approach to these substances very important for human health as well as for animals. Regular health monitoring regarding POPs pesticides does not exist.

**CONCLUSION**

In order to become a credible candidate for EU membership, we have to manage the pesticides in an appropriate manner. Therefore, we will have to first adopt all the required legislation pertaining to pesticides production, distribution, application and residues in the foodstuff, soil, water, air and biosphere as a whole.

**REFERENCE**


**ABSTRACT**

In Bosnia and Herzegovina, before and during the war, obsolete pesticides were used for pest control, but there are no records on exact quantities that were applied. The annual consumption of all groups of pesticides was 2500 metric tons. In Bosnia and Herzegovina there is no the pesticides production of any kind. The Legislation regarding pesticides has not yet been fully developed.

*Key words: Consumption, food, land, pesticides, residue.*
PCDD/PCDF CONTAMINATION FROM HISTORICAL PESTICIDE USE AND PRODUCTION – A CASE STUDY USING DATA FROM JAPAN AND GERMANY

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ABSTRACT

Pesticide use and deposition of pesticide production residues contribute to environmental PCDD/PCDF contamination, in particular on a historical scale. Despite potentially substantial quantities of PCDD/PCDF emission, and remaining depositions via this route, only limited information is available on the resulting environmental contamination load or pathways. The total dioxin emission from the use of pesticides in Japan during the past 40 years (1955-1995) was estimated to 540 tonnes of PCDD/PCDF or 250 kg of TEQ from PCP (with predominant OCDD/OCDF and other highly chlorinated congeners), and 380 tonnes of PCDD/PCDF or 210 kg TEQ from 2,4,6-trichlorophenyl-4′-nitrophenyl ether (CNP) (with 1,3,6,8/1,3,7,9-TCDD as dominant congeners).

The PCDD/PCDF impurities from PCP and CNP pesticides still contribute a large part of today’s PCDD/PCDF contamination in Japanese soil and sediments. A comparison of PCDD/PCDF loads derived from PCP/CNP application and their deposition in sediments of the Tokyo bay showed that only a small portion of PCDD/PCDF agrochemical impurities have been deposited in the Tokyo Bay sediment during the past 45 years. This indicates that a large part of the PCDD/PCDF load still exists in the terrestrial soil or river sediments of this area, which results in future runoff into Tokyo Bay. This highlights the pertinence of assessing pesticide contamination and application history for the understanding of environmental PCDD/PCDF loads and risk assessment.

Information from former pesticide production sites and associated landfills present another example for emissions of large quantities of PCDD/PCDFs to the environment in the past and future. In particular, the residues from production of various chlorinated pesticides (e.g. 2,4,5-T, PCP, PCP-Na, HCH1) were contaminated with high concentrations of PCDD/PCDFs and were found to leach from deposits together with pesticides, other chlorinated aromatics and aliphatics. This highlights the necessity of monitoring, containment and possibly remediation of such hotspots.

The present paper summarises and discusses available data and estimates from two case studies in Japan and Germany on pesticide application and production-derived PCDD/PCDF contamination in order to highlight the potential significance of such, predominantly past actions, to environmental PCDD/PCDF loads of the future.

Key words: PCDD, PCDF, pesticide, PCP, 2,4-D, 2,4,5-T, HCH, CNP, chloralkali electrolysis, remediation.

INTRODUCTION

The Stockholm Convention is a global treaty aimed to protect environmental and human health from contamination with persistent organic pollutants (POPs (Stockholm Convention (SC) 2001). At present the most notorious 12 POPs are included in the list of the Stockholm convention, 8 of which represent pesticides (SC 2001). Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) are also included in the Stockholm Convention as unintentionally formed POPs (Article 5/Annex C) (SC 2001). Today the scientific discussion on PCDD/PCDF sources focuses mainly on thermal emissions (e.g. waste incineration, cinder plants, secondary metal production), however, the history of PCDD/PCDF contamination is closely related to the chlorine industry and the production and use of chlorine and chlorinated organics including chlorinated pesticides2 (Weidenbach et al. 1984, UNEP 2005). “Highlights” of the “PCDD/PCDF history include contamination from pesticide production and use (in particular from 2,4,5-T/2,4,5-T3CP production).

Pesticide production was found to result in high exposure and contamination of workers (Degler and Uentzelmann 1984, Weidenbach et al. 1984, Dohmeier and Janson 1983, Schecter 1994). In addition, the application of PCDD/PCDF containing 2,4,5-T agents in the Vietnam war (Stellmann et al. 2003) contaminated large areas in South East Asia, including local populations and spraying personnel ((Degler and Uentzelmann 1984, Dohmeier and Janson 1983, Weidenbach et al. 1984, Stellmann et al. 2003). Also the

1 High concentration of PCDD/PCDF (46 g/kg) were present in residues from HCH degradation for chlorobenzene production of the factory in Hamburg (Degler and Uentzelmann 1984).
2 Some emission factors for relevant pesticides are listed in the “Standardized toolkit for identification and quantification of dioxin and furan release” (UNEP 2005).
public discussion and awareness on PCDD/PCDF was finally initiated by a heavy accident at a 2,4,5-T 3CP production site 1976 in Seveso (Mocarelli 2001). The actual release of PCDD/PCDF to land via waste from pesticide production, however, is not clear. Wenborn et al. (1999) estimated the release of PCDD/PCDF from pesticide production to 160 to 26500 g/year (Wenborn et al. 1999)3. The wide range of the estimation is indicative for the lack of data required for a clear determination of emission factors. Since pesticides were a major PCDD/PCDF source in the past, PCDD/PCDF emissions from these sources have already been distributed and disposed of. Due to the persistence of PCDD/PCDF, however, the burden of “historical” pesticides use and production may still represent a key source to the environment and humans today and into the future through runoff from soil and sediments, leaching from deposits (landfills, dumps, unsecured stockpiles), existing contamination/exposure in contaminated regions and former and potentially present application of contaminated pesticide stockpiles in developing countries.

There remains little research focus on these topics and, consequently, only limited information is available to date that would allow an estimate on the total share of pesticides to the global PCDD/PCDF burden and contamination flux. Hence it is not possible to evaluate their actual impact on environmental contamination and their fate with respect to wildlife and human exposure at present and in the future.

In recent years, the total historic release of PCDD/PCDF from pesticide use was investigated and assessed for Japan (Masunaga 2004, Masunaga 2001a, Ogura et al. 2001). In addition, the relevance of PCDD/PCDF contamination from former pesticide production sites was revealed during an investigation and remediation attempt of former pesticide production sites and associated landfills/areas in Germany (Universität Bayreuth 1995, Degler and Uentzelmann 1984, Schnittger 2001, Otto 2005). These “case studies” provide an overview on the subject and the current paper aims to illustrate the relevance of (predominantly) historical pesticide contamination for PCDD/PCDF emissions to the environment through their application and production. Experiences with remediation of pesticide production and disposal sites are presented and the challenges involved with this past legacy are discussed.

RESULTS AND DISCUSSION

1. Dimension of PCDD/PCDF release from historic pesticide production

1.1 Concentration of PCDD/PCDF in pesticides

The fingerprint and amount of PCDD and PCDF impurities in agrochemicals were studied by trace analysis of historic Japanese pesticide formulations in order to evaluate the contribution of historical pesticide use to environmental PCDD/PCDF contamination (Masunaga et al. 2001, Seike et al. 2003). The chemicals analysed include pentachlorophenol (PCP) (Table 1), 2,4,6-trichlorophenyl-4’-nitrophenyl ether (chloronitrofen CNP), 2,4-dichlorophenyl-4’nitrophenyl ether (nitrofen, NIP), tetrachloro-iso-phtalonitrile (chlorothalonil, TPN), and 2-methyl-4-chlorophenoxyacetic acid (MCP) and recently produced 2,4-dichlorophenoxyacetic acid (2,4-D). Two herbicides, PCP and CNP, produced during the 1960s and 1970s, contained elevated concentrations of PCDD/PCDF and TEQ.

![Table 1. PCDD/PCDF concentration in Japanese agrochemical pentachlorophenol samples (concentration calculated to gram active ingredient)](image)}

(a) Masunaga et al. 2001; (b) Seike et al., 2003

3 The estimated contemporary release from 55 countries (national inventories for emission to air from 22 countries (10370 g) and total release from 23 countries using the toolkit approach (9770g)) amounted to 20140 g (Fiedler 2005).
1982 the Dioxin content of CNP decreased due to the change of production processes resulting in an average concentration of 710 μg PCDD/PCDFs/g and 0.022 μg WHO-TEQ/g active gradient for post-1982 produced formulations (N= 23 samples) (Masunaga et al. 2001, Seike et al 2003, Yamagishi et al. 1981, Morita 1991, Mitsui Chemicals 2002). In contrast to CNP, no specific time trend could be observed for PCP and high PCDD/PCDF concentration were still detected in samples produced during the end of the 1970s (Table 1). The average dioxin content in PCP (N= 14 samples) was 3,300 μg PCDD/PCDF/g and 1.50 μg WHO-TEQ/g active ingredient (Table 1) (Masunaga et al. 2001, Seike et al. 2003, Mitsui Chemicals 2002). The remaining pesticide formulations investigated contained comparatively low concentrations of PCDD/PCDF (Masunaga et al. 2001).

1.2 Estimation on total PCDD/PCDF emissions from Pesticide use in Japan

The total dioxin emission from the application of pesticides in Japan during the past 40 years (1955-1995) was estimated based on the arithmetic average concentration of PCDD/PCF in historical pesticides and amount of pesticides used (see 1.1). The total emission from PCP use was estimated to 540 tonnes of PCDD/PCDF (with predominant OCDD/OCDF and other highly chlorinated congeners) or 250 kg of TEQ\(^4\). The total emission from CNP use was estimated to 380 tonnes of PCDF/PCDF (with 1,3,6,8/1,3,7,9-TCDD as dominant congeners) or 210 kg TEQ\(^4\). These loads contribute a large part of today’s PCDD/PCDF contamination in Japanese soil and sediments. In comparison to the total release of PCDD/PCDFs from waste incineration, today’s key PCDD/PCDF emission source representing approximately 90% of PCDD/PCDF emissions in Japan, the estimated total release of PCDD/PCDFs from pesticide use is considerably higher (Figure 1). This highlights that historical pesticide use represents a key contributor of PCDD/PCDF contamination in Japan.

1.3 Mobility of PCDD/PCDFs from former pesticide use

- trend and sources of dioxin pollution in Tokyo Bay

One key question, currently still unresolved, with regards to assessing the past and future environmental PCDD/PCDF contamination (and hence food web cycling and human exposure) is the mobility of POPs and pesticides deposited in landfills, dumps, uncontained storages and soils and sediments (Figure 2). A comprehensive study on historical PCDD/PCDF load and their transport to rivers and ocean sediments has been performed for the Tokyo Bay basin (Masunaga 2004). For this task, the dioxin load to Tokyo Bay basin was estimated from the annual quantities of agrochemical shipments to Tokyo, Saitama, Chiba and Kanagawa Prefectures (Ministry of Agriculture, Forestry and Fishery, 1959-1996), the percentage of prefecture area belonging to the basin, and the dioxin contamination of the agrochemicals.

The total PCDD/PCDF load to Tokyo Bay basin during the past 45 years from PCP was estimated to be approximately 31,000 kg PCDD/PCDFs and 14 kg TEQ. Those from CNP were estimated at 9,300 kg PCDD/PCDFs and 5 kg TEQ. Assuming that annual PCDD/PCDF deposition from combustion sources did not vary much during the past 45 years, the estimated recent average deposition in the Kanto region (Ogura et al. 2001) was used to as the average deposition of past years to calculate the basin-wide load from atmospheric transport of PCDD/PCDF contamination to the basin.

\[\text{(1)}\]

\[\text{The average TEQ value is in good agreement with the emission factor of 2,000,000 μg TEQ/t listed in the “Standardized toolkit for identification and quantification of dioxin and furan release” (UNEP 2005).}\]
The bulk production of chlorinated pesticides are often associated with a substantial amount and environmental emission of PCDD/PCDF from pesticide production. The total amount of PCDD/PCDFs deposited in sediments of Tokyo Bay during the same period was estimated from sediment core data with horizontal corrections based on surface sediment data (Masunaga 2004) (Table 2). A comparison between the total PCDD/PCDF emissions and sediment load in Tokyo Bay shows that only a few % of PCDD/PCDFs applied to paddy fields as agrochemical impurities have been deposited in Tokyo Bay to date.

Due to the persistency of these compounds, the remaining PCDD/PCDF portion still exists in the terrestrial soil or river sediments, providing an input source to Tokyo Bay into the future. Similarly, a relatively long time lag has been observed in Tokyo Bay sediment cores, where sediment PCDD/PCDF concentrations (derived from PCP and CNP) peaked during the mid 1960s and the beginning of 1970s, but in particular PCP derived PCDD/PCDFs still contributed a large proportion to the total TEQ in most recent sediment layers (Figure 3). According to the concentration of PCDD/PCDFs in Tokyo Bay sediments, the flux from PCP originating PCDD/PCDFs remained constant over the past 20 years (Figure 4). This indicates that PCDD/PCDF transport processes in the environment may last for decades (and most likely centuries), and will impact on the environment of future generations.

### 2. PCDD/PCDF in residues from pesticide production

#### 2.1 PCDD/PCDF in residues of pesticide production

Residues from production of various chlorinated pesticides (e.g. 2,4,5-T, PCP, PCP-Na, HCH1) represent another source of release of large PCDD/PCDF quantities. While these pesticides have been produced around the world, not many cases are documented on total PCDD/PCDF contamination of disposed residues. However, two cases in Germany gained public and political attention (and therefore detailed investigations) demonstrated that considerable amounts of PCDD/PCDF were released in residues from pesticide production (Degler and Uentzelmann 1984, Universität Bayreuth 1995, Lutz 1991, Thater 1996, Otto 2005). The total contamination from pesticide production residues (predominantly 2,4,5-T and HCH1 and other chlorinated organics) from one German factory in Hamburg during ca. 30 years was estimated to 377 kg TEQ3 (Universität Bayreuth 1995); these residues were deposited on nearby landfills and the production area.

In the second case, contamination from residues of a PCP and PCP-Na production in Rheinfelden (South Germany) was estimated to 7 tons of PCDD/PCDF (preliminarily OCDD) and 7.7 kg TEQ mainly from PCP-Na production (Otto 2005, Schönberger 2005). In addition, the area was heavily contaminated with PCDD/PCDF from deposited residues of a chloralkali electrolysis facility3 (8.5 kg TEQ) (sludge from electrolysis cells resulting mainly from reaction of chlorine with the pitch binder of graphite anodes – Lutz et al. 1991). The total PCDD/PCDF amount deposited from PCP/PCP-Na production and chloralkali electrolysis amounted to 16.2 kg TEQ3 (Otto 2005).

There are vast numbers of former production sites of 2,4,5-T, PCP, other chlorinated aromatic pesticides and HCH1 around the globe (often associated with chlorine production via chloralkali electrolysis). Similar high PCDD/PCDF contamination for these sites is probable and similar burdens in (typically nearby) landfills and water sheets can be expected. However, the deposited PCDD/PCDF quantity depends in addition to the products itself also on the production process of the respective pesticide and some other key factors. For example, the key factors determining the amount and environmental emission of PCDD/PCDF from

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*Table 2. Mass balance of dioxins in Tokyo Bay basin between 1951 and 1995*

<table>
<thead>
<tr>
<th>Source</th>
<th>Load to basin kg</th>
<th>Amount existed in sediment kg</th>
<th>Run-off rate</th>
<th>Load to basin g TEQ</th>
<th>Amount existed in sediment g TEQ</th>
<th>Run-off rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCP</td>
<td>51,000</td>
<td>156</td>
<td>2.5</td>
<td>14,000</td>
<td>1,290</td>
<td>8.6</td>
</tr>
<tr>
<td>CNP</td>
<td>2,500</td>
<td>144</td>
<td>7.5</td>
<td>1,000</td>
<td>65</td>
<td>3.3</td>
</tr>
<tr>
<td>Combustion</td>
<td>42*</td>
<td>150</td>
<td>(39)***</td>
<td>460</td>
<td>950</td>
<td>(23)***</td>
</tr>
<tr>
<td></td>
<td>34***</td>
<td></td>
<td></td>
<td>3,600***</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Direct deposition to seawater surface in Tokyo Bay; ** Deposition to terrestrial basin; *** Run-off rate for load to terrestrial basin.
2,4,5-T production include the synthesis methods and production temperature, whether PCDD/PCDFs are separated from the pesticide product (resulting in contaminated residues which may be reused) and finally, whether residues are destroyed in hazardous waste incinerators or placed into landfills. Therefore, the (former) production processes and waste management practice have to be considered for evaluating the potential relevance of PCDD/PCDF contaminations from respective production site and associated landfills. In addition, PCDD/PCDF loads from such activities have to be assessed for the evaluation of their contribution to environmental PCDD/PCDF burdens. Finally, the assessment of PCDD/PCDF loads and the environmental relevance from such sites requires evaluation based on actual measurements.

2.2. Leaching of PCDD/PCDF and pesticide/pesticide residues from landfills and deposits

To date, only limited information exists on the potential of residue contaminant leaching from landfills to ground water over extended periods of time. While PCDD/PCDFs are typically considered the least mobile of contaminants, due to physico-chemical properties, experiences from the former pesticide production site and related landfills in Hamburg revealed that PCDD/PCDF, the pesticides residues and other chlorinated aromatics and aliphatics can leach readily from such sites depending e.g. on the quality of the landfill, the geological conditions and other wastes co-deposited with the PCDD/PCDF and pesticide residues.

The high concentrations of (chlorinated) organics in leachates from this type of landfills support the leaching of PCDD/PCDF from the landfill and concentrations of 2,3,7,8-TCDD up to 75000 ng/kg were detected in oily leachates from one landfill (Schnittger 2001). This case highlights that leachates and ground water around landfills/dumps and hot spots of former pesticide production sites have to be monitored for contaminants including PCDD/PCDFs.

2.3 Remediation of contaminated production sites and associated landfills

The remediation of soils and sediments impacted from use of pesticides (and PCDD/PCDF contaminants) seems impossible due to the wide distribution and dilution in the environmental compartments and will therefore continue to impact environment and humans (Figure 2). However, the remediation or containment of former production areas and associated landfills (pesticide production and other chemical production) is a contemporary issue e.g. in Germany (see below, Schnittger 2001) and Switzerland (BCI 2005; Forter and Walther 2004) and will remain an important global task in the future. The remediation and containment of the above discussed pesticide production areas and associated landfills in Hamburg and Rheinfelden are ongoing to date and can be viewed as one of worldwide precedent cases.

One key conclusion that can be drawn is that it remains difficult and cost extensive to completely remediate contaminated areas due to the large volume of contaminated soils and landfilled materials. In Hamburg a complete remediation of the contaminated areas was considered relatively unfeasible due to the estimated costs (although the sites are inside the city) resulting in primarily containing the contaminated areas. Even the remediation of some hot spot areas in this case, the break down of production buildings, containment of the production area and related landfills and the measures for minimization of contamination of ground water resulted in expenditures in the order of several hundred million EURO by the responsible company.

Similarly, in Rheinfelden (South Germany), several landfilled sites were heavily contaminated by PCDD/PCDF. In addition wide areas of the city were/are impacted by PCDD/PCDF since contaminated solid residues were filled in gravel-pits, which arose at many individual estates to gain construction material. Therefore, the entire inner city of Rheinfelden (ca. 290 ha) had to be evaluated (1916 estates) including the analysis of soil samples from 729 estates and the establishment of a detailed “soil map” of the city (Thater et al. 1996). Heavy contaminated soil (> 1000 ng TEQ/kg) was substituted and removed, and in some cases was contained by removing of the top soil, fitting a geo textile and cover the bottom soil again with non-contaminated soil. A total of 36 estates/contaminated sites have been remediated. However, still an assessment has to be carried out for any new construction activity within the town today and in future (Otto 2005).

All 36 “hot spot estates” with a PCDD/PCDF-contamination of more than 1000 ng TEQ/kg have been remediated, whereas estates with a contamination below this value remain without actions, however, agricultural use of estates with a PCDD/PCDF-contamination of more than 40 ng TEQ/kg is not allowed. Against this background, also for Rheinfelden a complete remediation of the contaminated areas (landfills, production site and lower impacted estates) was considered not feasible due to the high cost. However,

---

6 Switzerland exemplifies the requirement of total remediation of chemical waste landfills (based on a polluter pays principle). Two large scale remediation projects are currently undertaken in Kölliken (estimated remediation cost 500.000.000 SFr) and Bonfol (estimated remediation cost 300.000.000 SFR). (Forter and Walther 2004, BCI 2005).

7 Other cases are e.g. treated in US in the frame of the Superfund site (US EPA 2005) and the above mentioned cases in Switzerland.

8 In several cases, highly PCDD/PCDF-contaminated sludge from chloralkali cells has been dumped in such gravel-pits also.
the containment of the former landfills and soil contamination on the production site could minimize the risk of further environmental contamination in Rheinfelden (and Hamburg). Furthermore, responsible and rational management of the contaminated estates inside the town could minimize the risk of health impact on the population of Rheinfelden (Otto 2005, Schönberger 2005, Thater et al. 1996).

Some conclusions and experiences with remediation and secure containment of former chlorinated pesticide production sites and associated landfills in Germany are:

- Detailed documentation of former production processes of the facility and transparency of type, amount and location of waste residues from these productions are important.
- Landfills and contaminated areas (based on detailed data from historic documentation) need to be localised.
- Assessment of the landfills and contaminated area:
  - Extent of contamination,
  - Geological conditions and frame of the sites,
  - Actual contamination/contamination risk of ground water;
- Mobility of contaminants.
- Close cooperation of the pesticide/chemical company and state/local authorities is required; open communication with impacted public and NGOs is required.
- Extent and type of PCDD/PCDF contaminants in production residues and therefore at production sites (including buildings) and associated landfills need to be evaluated.
- Experienced engineering offices qualified in the field of remediation of contaminated areas of similar type should be consulted. The planning needs high creativity since the solutions applied are normally not the standard engineering techniques but might be rather unique.
- Priority setting after comprehensive environmental impact assessment, overview on contamination and available remediation funds.
- Specific safety guidelines for worker protection are inevitable. The supervision of the building/remediation site needs special care.
- Comprehensive evaluation of remediation technologies – wrong choice of technologies can lead to enormous costs and project delay.
- Secured landfills and secured production sites are constructions not made for “eternity” but built for a limited time which need to be controlled, supervised and potentially repaired/renewed9. Furthermore the leachates and the ground water need possibly continuous remediation and supervision. These activities result in high maintenance costs, which have to be paid for decades, most likely centuries (millennia?) to come.
- Assessment if total remediation of the area is possible and necessary4.
- Timely environmental impact assessments and then prompt remedial and securing actions can minimize total damage and costs.
- Evaluate how and to which extent the “polluter pays principle” can be applied.

CONCLUSIONS
A large percentage of today’s PCDD/PCDF loads in the environment (soil, sediments, former production sites, associated landfills and other hot spots) originate from pesticide use and pesticide production. For Japan, the largest source of PCDD/PCDF release into the environment resulted from historical pesticide use (Figure 1). The contamination of the same type of pesticide varied depending on the time of production and the production process. It was discovered that not only well known key pesticides like PCP can contain high PCDD/PCDF concentrations but that also lower chlorinated pesticides like 2,4,6-trichlorophenyl-4′-nitrophenyl ether (CNP) can contribute high levels of PCDD/PCDF to total environmental burden.

While the information on CNP use is limited to Japan, it is known that PCP and other potentially PCDD/PCDF contaminated pesticides (e.g. 2,4-D, 2,4,5-T, other chlorinated aromatic pesticides) were used worldwide. Therefore the assessment of impurities in former chlorinated pesticides and the amount and pattern of pesticide use is one key of understanding PCDD/PCDF contamination of soils and sediments in a country and for global contamination. In this respect the relevance of PCDD/PCDF contamination of pesticide stockpiles may additionally be considered/evaluated. Further, for the final destruction of pesticide stockpiles the risk of PCDD/PCDF formation and emission have to be considered, evaluated and monitored (Weber 2005).

A further significant PCDD/PCDF burden to the environment associated to chlorinated pesticide production stem from land filling of production residues and the contamination of the production area and buildings. The contaminations from production residues are normally restricted to hot spots at production sites and associated landfills but can possibly impact extensive local regions including residential areas (such as Rheinfelden). From experiences in Germany these former pesticide production sites, related landfills and other impacted areas can be contaminated with tons of PCDD/PCDF and hundreds of kg of TEQ9 if specific chlorinated aromatics (e.g. PCP-Na, 2,4,5-T or HCH9) were in the production portfolio.

The remediation and/or securing of this type of area remain a difficult but important task and should be considered as one priority in the action planning of national implementation plans of the Stockholm Convention. The current impossibility of comprehensive remediation of contaminated areas and landfills, the possibility for leaching of the contaminant, the difficulties of containing these sites and the tremendous costs of these projects demonstrate that land filling of hazardous waste creates large burdens for environment and society (in the future) which can not be accepted for the sake of future generations and when acknowledging the principle of sustainable development.

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Japan), Y. Yao (Testmark Laboratories Ltd. Canada), and H. Takada (Tokyo University of Agriculture and Technology, Japan), W. Otto (Landratsamt Lörbach, Germany), H. Schönberger (Landespräsidium Freiburg, Germany) and H. Wirth (Behörde für Stadtentwicklung und Umwelt, Hamburg, Germany).

REFERENCES

HCH RESIDUES IN SOME FRESH WATER, SEDIMENT AND IN SOME AQUATIC ORGANISMS IN TURKEY
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Hacettepe University, Science Faculty, Department of Biology, Beytepe Campus, 06532 Ankara, Turkey

ABSTRACT
The widespread use of synthetic organic pesticides over the past half-century has led to their detection in many hydrologic systems of the countries. Pesticides, as well as agricultural and industrial toxic chemicals are complex mixtures of isomers and congeners, which have been detected in air, water, and in biota all over the world. Pesticide’s contamination of surface water, sediments and groundwater from agricultural use has been well documented around the world. The widespread use of pesticides for agricultural and non-agricultural purposes has resulted in the presence of their residues in various environmental matrices. Organochlorined Pesticides such as HCH and its isomers are known to resist biodegradation and they can be recycled through food chains and produce a significant magnification of the original concentration at the end of the chain. Due to long residence time of these substances in the environment, there is a great interest in examining the pollution they cause. Their use has been prohibited in Turkey as well as in other countries, after evidence of their toxicity, persistence and bioaccumulation in the environment became known. The determination of pesticide residue in water sediment and fish samples is necessary.

HCH was analysed in:
• water, sediment, blue carp, two fish species (carp and grey mullet) and water birds (Fluca atra, Anas platyrhynchos and Egretta garzetta) in the Göksu delta,
• water and sediment in Manyas Bird Lake,
• water, sediment and fish (Cyprinus carpio) in Upper Sakarya basin,
• water, sediment and fish species (bleak, carp and wells) in Sariyer Dam Lake,
• water, sediment, blue carp and fish species (Capoeta capoeta, Oreochromis mosambica, Liza ramada, Chelon labrosus and Anguilla anguilla) in the Köycegiz Lagoon system,
INTRODUCTION

The use of synthetic organic compounds, such as organochlorine pesticides, was widespread in the world between the 1940s and 1985. The increased use of various types of pesticides in the past, particularly organochlorine pesticides, has led to concern regarding the potential for contamination of environmental media (i.e., water, sediment and biota) and associated effects on human health and wildlife (Kolankaya, 2004). Being persistent, traces of organochlorine compounds could be the result of either recent use or of long duration (Kolankaya, 1984; Das et al.2002).

One group of organochlorine compounds is HCH that was used in agricultural activities in Turkey. Hexachlorohexane is an effective insecticide by contact and in digestive and respiratory systems of pests. It is a wide spectrum insecticide used in animal ectoparasites, soil endemic insects, public health diseases, and predators. HCH is a widespread contaminant that has entered the environment through its past manufacture and use as a pesticide and its formation as a by-product during the production of a variety of chlorinated compounds. HCH was restriction in 1978 and then banned in 1985, whereas lindane was banned in 1979.

Status of pesticides placed in POPs list in Turkey

After the restriction and ban of use of POPs pesticides in some countries, necessary precautions were taken in Turkey. Starting from 1978 the use of aldrin, dieldrin, heptachlor, DDT, chlordane and toxaphene were restricted. Application of soil with aldrin and heptachlor was forbidden, but application on seed was allowed. There were no restrictions on HCB during those years. However, after some applications, HCB residues were found on weeds and DDT residues were found in straw (Güvener et al., 1974). Hexachlorobenzene, α-HCH, γ-HCH (lindane), foodstuff analyses and water samples.

Analysis of the regional database showed that among the twelve POPs, HCH or BHC included in the Stockholm Convention. A literature survey as background material for the assessment was used, performed for the candidate involved in the study, and covering the years 1977-2004. DDT, aldrin and BHC were those accumulating to a higher number of references (Kolankaya, 2005).

According to Turkish codex the limit values for organochlorine pesticides include BHC are below 0.0005 mg/kg for fat and below 0.0001 mg/kg for meat. The residue values found in the study was 1/4 of the limit values in codex (Refik Saydam Hygiene Institute and Kolankaya, 2005).

In this presentation 17 studies deal with HCH and lindane residue in water, sediment and biota in different area (Black Sea, Marmara, Aegean, Mediterranean and Central Anatolia regions in 1971-2004).

Hexachlorohexane and γ-BHC (lindane) is a wide spectrum insecticide used in animal ectoparasites, soil endemic insects, public health diseases and predators. Along with those applications, hexachlorobenzene (2.6%) can be used with fungicides in seed applications (Güvener, 1974).

Pesticide residue was analysed in six different locations and years (in 1971-1973) of Black Sea water. γ-BHC was found in all station, the amount was 0.24-2.42 ppm. Other isomers of BHC were found at some stations, values were 0.06-3.29 ppm in 1971-1973. In another residue determination study, performed by the same group in fish in the Black Sea region in 1975, residue levels were found as mean 0.074 ppm BHC isomers. The total insecticide level was calculated to be 0.409 ppm (Telli, 1991).

The first analyses were carried out in samples of water, sediment, soils and biota in Göksu Delta. As a result of the...
study, BHC and their isomers were detected in water and sediment samples of Göksu Delta (residues ranging from 0.007 lindane in water to 0.684 α-BHC in sediment). BHC was analysed in blue carp two fish species (carp and grey mullet) and water birds (Fluca atra, Anas platyrhynchos and Egretta garzetta) - data shown in table 1 and 3 (Ayas, Barlas, and Kolankaya, 1997). α-BHC residue was higher than others in water, sediment and also agricultural soil and dune area samples. Amount of lindane was higher in agricultural soil and sediment.

The amount of BHC values were higher than water and soil in biota, particularly were fat tissue contain high concentrations, than others like liver. The highest residue was found in the fat tissue of water birds.

**Mediterranean study area located in the Dalyan district of Mugla.** All samples were collected between October 1992 and February 1994 in Köycegiz Lagoon system. Water, sediment, carp and some fish samples were analysed. Small amounts of α-HCH, β-HCH and γ-HCH were determined in blue carp samples. The highest concentration was observed in γ-HCH. Mean levels of α-HCH, β-HCH and γ-HCH were observed in all the fish samples analysed and the highest concentrations fish species muscle tissues were γ-HCH in O.mossambic (35.90ug/kg) L.ramada (26.30 ug/kg),C. capoeta (6.75ug/Kg), C. labrosus (5.33ug/kg) and HCH was not found in water and plankton samples, but was determined in sediment samples. The residue level is lower in blue carp tissue than in fish tissue (Çalýskan and Yerli, 2000). Similar results have been found in carp and fish samples from Göksu Delta in Mediterranean coast.

Manyas Lake-Balikesir (known as the “bird paradise”) and its basin during November 1996 and May 1997. Contamination level of the water is above the threshold toxic level for the aquatic fauna and flora, when compared to Turkish regulations (Kolankaya et al., 1997). The contamination level was higher in the lake than in the surrounding fresh waters Manyas Lake is contaminated by different types of pesticides. Organochlorine pesticides were detected in sediment and water samples taken from eight different stations in Manyas (Table 3).

Water samples from the distribution area were also analysed and only α-BHC residues were found in the tap waters of several districts. Several raw and potable water samples from the drinking water supplies of Istanbul were analysed for the nine organochlorine pesticides. Only α and β-BHC and aldrin were detected in GC and TLC analyses. Amount of α-BHC was found between 0.142 ± 0.003 to 0.886 ± 0.013 ppm. Amount of γ-BHC was not found.

Since they are persistent enough and degraded very slowly they easily accumulate in the soil. The pesticide concentration in the reservoir water is related to the partition coefficient at kinetic equilibrium involving sorption and de-sorption processes (Aydin and Yurduń, 1999).

Different isomers of BHC residue were determined water in agricultural area around of two rivers (Kizil irmak and Yeğil irmak) of Black Sea Coast (Table 4). Different isomers of BHC concentrations determined in mussels samples from the Mid-Black Sea Coast of Turkey in 1999 and 2000 shown in table 5. It has been shown that BHC concentration was decreased in last years after banned these pesticides in Black Sea surface water compared with 1971-1973.

We compared with water and mussels sample were found highest concentration of beta HBC in mussels in all stations than water. Residues of BHC isomers are stiles detectable levels in this region because very high concentration used in the past for agricultural activities.

Five different OC pesticides and their degradation products were detected in sediment, water and fish in the upper Sakarya basin (Barlas, 1999). α-BHC, β-HCH and lindane were detected in October 1995 only α-BHC was detected all sampling time but the others were not detected in 1996 α-HCH, β-HCH and lindane were found in water, sediment and fresh mussel tissue of fish (Cyprinus carpio) at different stations in Sariyar Dam Lake. The amount of these pesticides was 0.018 ppm, only lindane in sediment to 0.048-

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### Table 1. Residue levels of organochlorine pesticides in water, sediment and various soil samples from Göksu Delta, 1993

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>Water Mean ppm N: 24</th>
<th>Sediment Mean ppm N: 24</th>
<th>Soil Agricultural area Mean ppm N: 16</th>
<th>Soil Non-Agricultural area Mean ppm N:16</th>
<th>Dune area Mean ppm N: 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-BHC</td>
<td>0.058</td>
<td>0.067</td>
<td>0.656</td>
<td>0.048</td>
<td>0.166</td>
</tr>
<tr>
<td>β-BHC</td>
<td>0.066</td>
<td>0.063</td>
<td>0.093</td>
<td>0.013</td>
<td>0.092</td>
</tr>
<tr>
<td>Lindane</td>
<td>0.007</td>
<td>0.164</td>
<td>0.256</td>
<td>0.115</td>
<td>0.087</td>
</tr>
</tbody>
</table>

### Table 2. Residue levels of organochlorine pesticides in carp, fish and water bird samples from Göksu Delta, 1993

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>Carp Mean ppm N: 24</th>
<th>Mullet Mean ppm N: 24</th>
<th>Mallard Mean ppm N: 16</th>
<th>Coot Mean ppm N:16</th>
<th>Egret egg Mean ppm N: 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-BHC</td>
<td>997</td>
<td>217</td>
<td>1165</td>
<td>1275</td>
<td>90</td>
</tr>
<tr>
<td>β-BHC</td>
<td>228</td>
<td>132</td>
<td>1165</td>
<td>2147</td>
<td>50</td>
</tr>
<tr>
<td>Lindane</td>
<td>1816</td>
<td>806</td>
<td>2153</td>
<td>1258</td>
<td>106</td>
</tr>
</tbody>
</table>

### Table 3. α-BHC and β-BHC residues in sediment samples of Manyas Bird Lake, May, 1996-1997

<table>
<thead>
<tr>
<th>Pesticides (ppb)</th>
<th>Sigircik Creek</th>
<th>Entrance of Sigircik</th>
<th>Kadare Creek</th>
<th>Kocaçay Entrance of Kocaçay</th>
<th>Dulkük Creek</th>
<th>Bereketli Creek</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-BHC</td>
<td>0.448</td>
<td>1.186</td>
<td>0.814</td>
<td>1.421</td>
<td>0.959</td>
<td>1.752</td>
</tr>
<tr>
<td>β-BHC</td>
<td>0.226</td>
<td>2.024</td>
<td>1.548</td>
<td>1.337</td>
<td>0.935</td>
<td>1.784</td>
</tr>
</tbody>
</table>

### Table 4. Different isomers of BHC concentrations determined in sea water samples 6 stations from the Mid-Black Sea Coast of Turkey in 1999 and 2000

<table>
<thead>
<tr>
<th>Compound</th>
<th>Baruthane Pg/ml</th>
<th>Yeşil Fener Pg/ml</th>
<th>Kırımaşı Fener Pg/ml</th>
<th>Belediye Evleri Pg/ml</th>
<th>Sinop Pg/ml</th>
<th>Yaliköy Pg/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-BHC</td>
<td>0.6</td>
<td>Nd</td>
<td>1</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>β-BHC</td>
<td>7</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>γ-BHC</td>
<td>Nd</td>
<td>0.3</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>δ-BHC</td>
<td>3</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
</tbody>
</table>

### Table 5. Different isomers of BHC concentrations determined in mussels samples 6 stations from the Mid-Black Sea Coast of Turkey in 1999 and 2000

<table>
<thead>
<tr>
<th>Compound</th>
<th>Baruthane Pg/ml</th>
<th>Yeşil Fener Pg/ml</th>
<th>Kırımaşı Fener Pg/ml</th>
<th>Belediye Evleri Pg/ml</th>
<th>Sinop Pg/ml</th>
<th>Yaliköy Pg/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-BHC</td>
<td>5</td>
<td>13</td>
<td>8</td>
<td>3900</td>
<td>190</td>
<td>50</td>
</tr>
<tr>
<td>β-BHC</td>
<td>12</td>
<td>13</td>
<td>8</td>
<td>ND</td>
<td>22</td>
<td>140</td>
</tr>
<tr>
<td>γ-BHC</td>
<td>3</td>
<td>18</td>
<td>8</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>δ-BHC</td>
<td>2</td>
<td>1</td>
<td>200</td>
<td>ND</td>
<td>ND</td>
<td>30</td>
</tr>
</tbody>
</table>

---

83
0.061 ppm $\alpha$-HCH in water. $\alpha$-BHC, $\beta$-BHC residues were found determination levels in adipose tissue of the bleak samples caught at Aladag Creek, Çayirhan, Usakbükü and Sariyar stations and $\alpha$-HCH and $\beta$-HCH also had considerable bioaccumulation levels (Ekmekçi et al., 2000).

BHC and isomers residue have been determined in water and sediment in Tuz lake, Hirfanli Dam lake, Eşmekaya lake, Tersakan lake and Bolluk lake in Central Anatolia. $\alpha$-BHC, $\beta$-BHC were detected in high levels in sediment samples. In Tuz lake, Hirfanli Dam lake, Esmekaya lake, Tersakan lake, Kozanlı lake and Kulu lake especially alpha BHC, beta BHC residues in water and sediment samples were generally higher than in other lakes, since they are located in wide agricultural areas. The highest amount of extractable alpha BHC was 1.38 $\mu$g/g (range ND – 2.719 $\mu$g/g mean) which was found in the sediment sample of Bolluk lake. Also the highest average amount of extractable beta BHC (2.328 $\mu$g/g mean of Hirfanli dam lake) was detected in sediment samples (Barlas, 2002).

Alfa, beta, gamma and delta isomers of BHC were determined in 16 samples of surface and ground water in the Middle Black Sea Region. The residue of BHC and isomers were found in six samples. Residue value was 0.0003-0.2505 $\mu$g/l in surface water, and 0.0001-0.572 ug/l in ground water in different isomers (Geyikçi and Büyükgüngör, 2002). Therefore, it is not possible to determine the environmental significance of the reported values.

Significant amounts of chloride pesticides and PCBs were found in the sea water and mussel samples are taken from the Black Sea, by Kurt and his team. Organochlorine pesticides include BHC and PCBs concentrations determined in mussel samples. Pesticides were coming from around two major rivers along agricultural activities in this region (Kurt et al., 2004).

The last study carried out in Meriç Delta in eight stations from water and sediment and five stations from fish fat tissue (Table 6 and 7). The analysed water samples showed the presence of the following organochlorine pesticide residues at concentrations above the method of detection limits. Concentrations of OC pesticides ranged from 0.466 to 1.127 $\mu$g/L for $\Sigma$ HCHs. Concentrations of OC pesticides in fish samples ranged from 725.57 to 1470.06 ng/g for $\Sigma$ HCH, 3.04 ng/g to 5.4 ng/g (Erkmen and Kolankaya, 2004).

### Table 6: Concentrations of HCH compounds in sediments (ng/g dw) at sampling stations from Meric Delta

<table>
<thead>
<tr>
<th></th>
<th>Station 1</th>
<th>Station 2</th>
<th>Station 3</th>
<th>Station 4</th>
<th>Station 5</th>
<th>Station 6</th>
<th>Station 7</th>
<th>Station 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ HCH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.313</td>
<td>0.297</td>
<td>0.213</td>
<td>0.723</td>
<td>0.77</td>
<td>0.38</td>
<td>0.703</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>(ND-0.94)</td>
<td>(ND-0.89)</td>
<td>(ND-0.64)</td>
<td>(ND-1.3)</td>
<td>(ND-1.67)</td>
<td>(ND-0.9)</td>
<td>(ND-1.6)</td>
<td>(ND-0.52)</td>
</tr>
<tr>
<td>$\beta$ HCH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>0.093</td>
<td>1.513</td>
<td>1.380</td>
<td>0.967</td>
<td>0.823</td>
<td>0.757</td>
<td>0.837</td>
<td>0.423</td>
</tr>
<tr>
<td></td>
<td>(ND-0.28)</td>
<td>(ND-2.29)</td>
<td>(ND-2.54)</td>
<td>(ND-1.779)</td>
<td>(ND-1.58)</td>
<td>(ND-1.25)</td>
<td>(ND-1.54)</td>
<td>(ND-0.88)</td>
</tr>
<tr>
<td>$\gamma$ HCH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.123</td>
<td>0.043</td>
<td>ND</td>
<td>ND</td>
<td>0.673</td>
<td>0.650</td>
<td>0.133</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>(ND-0.37)</td>
<td>(ND-0.130)</td>
<td>(ND-1.04)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta$ HCH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ND</td>
<td>1.31</td>
<td>1.093</td>
<td>1.063</td>
<td>0.437</td>
<td>0.62</td>
<td>1.487</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>(0.99-)</td>
<td>(1.7)</td>
<td>(0.83-)</td>
<td>(0.9-)</td>
<td>(ND-)</td>
<td>(0.18-)</td>
<td>(0.97-)</td>
<td>(0.16-)</td>
</tr>
<tr>
<td>$\Sigma$ HCH</td>
<td>0.406</td>
<td>3.243</td>
<td>2.679</td>
<td>2.753</td>
<td>2.703</td>
<td>2.407</td>
<td>3.16</td>
<td>1.073</td>
</tr>
</tbody>
</table>

### Table 7: Concentrations of different isomers of HCH in fish (Cyprinus carpio) (ng/g fat) at sampling stations from Meric Delta

<table>
<thead>
<tr>
<th></th>
<th>Station 1</th>
<th>Station 3</th>
<th>Station 4</th>
<th>Station 5</th>
<th>Station 7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n = 13</td>
<td>n = 12</td>
<td>n = 12</td>
<td>n = 16</td>
<td>n = 11</td>
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<tr>
<td>$\alpha$-HCH</td>
<td>545.48</td>
<td>319.5</td>
<td>957.75</td>
<td>327.58</td>
<td>968.15</td>
</tr>
<tr>
<td></td>
<td>(ND-1909)</td>
<td>(175-1377)</td>
<td>(ND-1829)</td>
<td>(ND-984)</td>
<td>(124-2089)</td>
</tr>
<tr>
<td>$\beta$-HCH</td>
<td>413.7</td>
<td>876.4</td>
<td>510.58</td>
<td>397.5</td>
<td>485.13</td>
</tr>
<tr>
<td></td>
<td>(174-1263)</td>
<td>(177-5640)</td>
<td>(ND-1953)</td>
<td>(105.7-376)</td>
<td>(149-918.5)</td>
</tr>
<tr>
<td>$\gamma$-HCH</td>
<td>0.86</td>
<td>2.49</td>
<td>1.73</td>
<td>0.49</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>(ND-2.24)</td>
<td>(2.5-17.5)</td>
<td>(ND-7.3)</td>
<td>(ND-4.2)</td>
<td>(ND-3.9)</td>
</tr>
<tr>
<td>$\Delta$-HCH</td>
<td>2.81</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>1.93</td>
</tr>
<tr>
<td></td>
<td>(ND-16)</td>
<td></td>
<td></td>
<td></td>
<td>(ND-7.6)</td>
</tr>
<tr>
<td>$\Sigma$ HCH</td>
<td>962.85</td>
<td>1198.39</td>
<td>1470.06</td>
<td>725.57</td>
<td>1456.89</td>
</tr>
</tbody>
</table>
It is evident that the proportions of HCH isomers in the fish samples reflect the technical mixture composition (approximately 65% α; 10% β; 15% γ HCH and 10% other isomers). Considering also the persistence order of these isomers (α < γ < β; 13), these results indicated that historical HCH input and a relatively recent use of HCH in the study area can be suggested as a possible explanation. Considering the groups of HCHs (HCHs = α-HCH + β- HCH +γ- HCH + λ-HCH) the predominance of α and β-HCH in all water, sediment and fish samples was clearly observed.

High HCH concentrations in analysed samples indicate usage of HCH as a pesticide in this region. Because the β-HCH isomer is the most persistent with respect to microbial degradation and has the lowest volatility, detection of β-HCH in soils, sediments and water is probably indicative of local technical HCH contaminants (Fernandes et al, 2000 and Kauras, et al. 2002).

CONCLUSION

This review focuses on HCH or BHC used in Turkey and residues in samples of various organisms and different environments obtained from the Black Sea, Central Anatolia the Aegean and the Mediterranean regions of Turkey. Some example studies have also been presented for inland water systems sediment and biota, including Göksu Delta, Köyceğiz Lagoon System, Sakarya basin, and Sariyar Dam Lake. HCHs residue determined only for water and sediment in Manyas Lake, a lake in Central Anatolia.

HCH isomers residues were found, all below toxic levels. High HCH concentrations in analysed samples indicate usage of HCH as a pesticide in this region with the past. Because the β-HCH isomer is the most persistent with respect to microbial degradation and has the lowest volatility, detection of α and β HCH in soils, sediments and water is probably indicative of local technical HCH contaminants (Fernandes et al, 2000 and Kauras, et al. 2002).

Since the year 1980, the increase in DDE/DDT ratio and decrease in ΣDDT and ΣBHC levels in water sediment and biota demonstrate that the influence of limitations and inhibitions for OCPs and the decrease of utilisation of these compounds in time.

When we consider DDE/DDT ratios, it is seen that the limitation and legislation for OCPs in Turkey has been effective and the exposure to these compounds tends to decrease in time.

Although the majority of organochlorine pesticides have not been used in Turkey for a long time, the residues of organochlorine pesticides are being observed in water sediment and aquatic biota strongly indicate that these pesticides have a persistent character to prevail in the environment for a long time without spoilage (Kolankaya, 2004).

REFERENCES

17. Refik Saydam Hygiene Institute, Poison Research Department’s Pesticide Residue Laboratories Analysis results between the years 1997-2004.
BIOACCUMULATION OF ORGANOCHLORINE COMPOUNDS IN EGGS OF TESTUDO HERMANNI BOETGERI (HERMAN’S TORTOISE) FROM THE IRON GATES NATURE PARK, ROMANIA

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University of Bucharest, Center for Environmental Research and Impact Studies

M. ZAHARIA
University of Bucharest, Department of Chemistry

C. HURA
Food Toxicology Laboratory, Institute of Public Health

ABSTRACT
A key aspect of the wildlife conservation programmes is the identification of threats that may endanger species perpetuation. The aim of this work was to evaluate the concentration of HCH and DDT isomers and residues, in terms of their metabolites in eggs of Testudo Hermanni, a protected species, living within Iron Gates Nature Park, in the southwest of Romania. The tortoise was the target of a conservation programme developed between 2001 and 2005. As it is an exclusive herbivorous species, it is highly exposed to contaminants that have been bioaccumulated in plants.

The eggs were collected from the natural nests and incubated afterwards. The analysed samples were from non-fer tile eggs (those eggs from which juveniles could not manage to form, hatch or develop properly) and they were analysed using a GC-ECD system.

INTRODUCTION
Organochlorine pesticides have been widely studied as far as their effects on the environment are concerned. Although the most toxic and non–biodegradable chemicals used as insecticides, herbicides or any other pest killer have been replaced with some more environmentally friendly substances, or have even been banned from being produced, there are still many traces of these chemicals, which were thought at a certain time, e.g. during the Second World War, as being a revolution in controlling pests as well as in controlling the agricultural crops from being damaged.1

Studies on HCH and DDT groups revealed important toxicological effects on terrestrial and aquatic species. This is mainly due to their persistency, toxicity and their ability to accumulate in live organisms, entirely or in their metabolites form. A detailed review on organochlorine pesticide effects on living organisms is performed by L. J. Blus – “Organochlorine Pesticides” in “Handbook of Ecotoxicology”.

Bioaccumulative nature is defined3 as being the characteristic that results in concentration of organochlorine pesticides in the biota, whether it is from water directly into an organism through gills, epidermis, and similar media (bioconcentration) or from food only (the food – chain effect of biomagnification). Bioaccumulation includes both biomagnification and bioconcentration. Studies suggest that intake from food is not the major source of residues from persistent organic pollutants in aquatic species.4 But it is the main source of persistent organochlorines for the most trophic levels in terrestrial systems.4

DDT, which was synthesized in 1874, is the best-known organochlorine. Discovery of its insecticidal activity by Paul Müller in 1939 led to his receiving the Nobel Prize.5 Highly toxic activities on terrestrial and aquatic ecosystems that have been proven subsequently have led to its complete prohibition many years ago. Still, traces of DDT and its metabolites, known as DDT group, can be found in environmental media.

Hexachlorocyclohexane (HCH) consists of a mixture of five isomers, out of which the gamma isomer (lindane) is the main insecticidal component.6 Lindane is one of the few organochlorines which is still widely used. Its presence in the environment presents a low risk compared to DDT group chemicals.3

The toxicity of organochlorines is highly variable, depending on species, sex, age, stress of various kinds and many other factors. For instance, LD50 ranges from 1 to more than 2080 mg/ kg in birds8 and 8 to 6000 mg/kg in laboratory rats.

Many protected species all over the world have been subjected to studies aimed at identifying the contamination by these highly toxic chemicals. Keller et al.9 reported positive analysis of HCH and DDE on sea turtles from North Carolina, USA. In addition, Willemessen and Hailey10 reported a study on the effects of herbicides on another protected species, Testudo Hermanni. Mortalities of wild animals, especially reptiles, have long not been associated with the use of pesticides.

Our study is aimed at identifying the level (if any) of organochlorine pesticides in eggs of Testudo Hermanni Boetgeri, a protected species belonging to the reptile category living in the southwestern part of Romania, within the Iron Gates Nature Park. It is an exclusively herbivorous species, a fact that limits the provenience of these toxic chemical compounds in living organisms from food, due to their well-know hydrophobic character and consequently, their very low concentration in water. As a result of a high depopulation11 processes, determined mostly by the human influence, the species was subjected to a conservation programme, aimed at increasing the number of the animals. Therefore, the eggs were collected from the natural nests and artificially incubated. Then, the tortoises were taken care of till they could survive in their own natural habitat and released back to where they...
came from. However, a number of eggs did not hatch successfully, or the juvenile could not develop properly. These eggs captured our interest, as a way to assess the impact of these chemicals to the reproduction of species, as well as their level of accumulation in living organisms.

**MATERIALS AND METHODS**

**Site description and field sampling**

The area from which the samples were collected is shown on the map below. The map presents The Iron Gates Nature Park, situated in the south-western part of Romania, at the border with Serbia and Montenegro. The species of tortoise living here prefers open areas, situated nearby forests or other wooded land\(^1\) and there is no correlation between tortoises and water resources. Consequently, following the possible habitats where tortoises could exist, there were four sampling sites: Bucov Valley, Tarov Valley, Mala Valley and Eselnita Valley. Actually, to meet the main aim of the project, namely reproduction of these endangered species, more sampling sites were necessary, but only eggs coming from these four areas proved to be non-fertile. Samples were collected from the natural nests, marked and incubated afterwards. The non-fertile eggs have been analysed afterwards. The eggs came from different tortoises, which were found and marked.

**Extraction of samples**

Measurements were made both on the inner core of the eggs and the eggshells. Therefore, extraction using light petroleum had been performed, followed by purification on fluorsyl column for both types of determinations.

**Contaminant analysis**

Analysis for organochlorine pesticide residues: DDT total [(op+pp') DDE, DDD, DDT] and HCH total (alpha, gamma, beta, delta) had been conducted using the gas-chromatographic method. A Carlo Erba GC-ECD, equipped with column, injector and detector was used for measurements. Carrier gas was nitrogen.

**RESULTS**

The results obtained for the analysis of each sample were processed so as the following plots were performed. Our aim was to see if there is constancy in the level of the accumulated pollutants, which pollutant has a higher potential of accumulation and which of the two parts of the egg can accumulate the highest concentration.

It should be noted that four isomers of HCH were tested for. As expected the highest levels were obtained for lindane - \( \gamma \) - isomer, which has been widely and largely used, for a long period of time in agriculture, although the area is not known as a very productive one, from this point of view. In some samples there were no traces of any isomers, but an average has been made to show the concentration levels in the region.

Furthermore, analyses were made for DDT as well as for its metabolites DDE and DDD. The interesting fact is that there was no trace of DDD in the samples, which led us to believe there is not an adequate medium for DDD formation, but a good environment for DDE to appear.

---

\(^1\) Reference to a specific area or location.
HCH concentrations

<table>
<thead>
<tr>
<th>Sampling Site</th>
<th>HCH Concentration (µg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bucovat</td>
<td>84</td>
</tr>
<tr>
<td>Mala</td>
<td>26</td>
</tr>
<tr>
<td>Tarovat</td>
<td>12</td>
</tr>
<tr>
<td>Eselnita</td>
<td>147</td>
</tr>
<tr>
<td>Inner core</td>
<td>8</td>
</tr>
<tr>
<td>Eggshells</td>
<td>9</td>
</tr>
</tbody>
</table>

Figure 2. HCH Total concentration for each sampling site

DDT concentrations

<table>
<thead>
<tr>
<th>Sampling Site</th>
<th>DDT Concentration (µg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bucovat</td>
<td>138</td>
</tr>
<tr>
<td>Mala</td>
<td>169</td>
</tr>
<tr>
<td>Tarovat</td>
<td>176</td>
</tr>
<tr>
<td>Eselnita</td>
<td>113</td>
</tr>
<tr>
<td>Inner core</td>
<td>165</td>
</tr>
<tr>
<td>Eggshells</td>
<td>40</td>
</tr>
<tr>
<td>Inner core</td>
<td>220</td>
</tr>
<tr>
<td>Eggshells</td>
<td>158</td>
</tr>
</tbody>
</table>

Figure 3. DDT Total concentration for each sampling site

**DISCUSSION**

*Distribution of OC-containing tortoises within the Iron Gates Nature Park*

From the very beginning of our discussion, it must be noted that there have not been detected polychlorinated biphenyls – PCBs, neither within the inner core samples, nor in the eggshells.

From the plots, it can be noted that, for all the sampling sites, the concentration level for DDT is higher than the HCH concentration level both in the inner core and the eggshells.

Moreover, the highest concentration of DDT is found to be at Eselnita, as expected, as it is the area mostly influenced by humans, and the usage of DDT as insecticide in the past is well known.

For hexachlorocyclohexane, one can note that it is a preferential accumulation in the core of the egg, as expected, as on one hand, the core content forms first and then the eggshell, which is not very permeable for these substances. On the other hand, the eggshell is mainly inorganic.

But for the DDT, one can observe a strange pattern for the area of Bucovat, namely that the concentration in the inner core is smaller than the concentration in the eggshell. One of the explanations for this anomaly can be that some of the samples collected from this area had already formed juveniles inside that never hatched. The analyses were made both on juveniles and the content left there, and an average was made. However, we can assume that DDT does not preferentially accumulate in organisms. We can assume that it passed to the eggshell during the formation of the juvenile.

When making a comparison, one notes that the level of concentration in the eggshells for HCH are much smaller than those of DDT, which leads to the assumption that DDT accumulates better in eggshells than HCH does.

**Provenience of the contaminants in the eggs of tortoises – possible paths of intaking**

First of all, the association of HCH with DDT is rooted in the fact that in the past in Romania, lindane (g - isomer of HCH) was used in a compound with other insecticides and fungicides, among which was DDT. There were several compounds, which were sold as single substances with different compositions and under their own names.²²

The investigated area is not a very agricultural area, therefore the presence of pesticides is a somewhat surprising. As it is an exclusively herbivorous reptile, the source of pesticides in tortoises is limited to food, as we have already stated earlier. The highest concentrations of them was expected to be found in the most populated area, namely Eselnita, but there are also fairly high concentrations in areas which are not populated and where the type of soil does not allow agriculture to develop.

Consequently, we can assume that the presence of the toxic chemicals in these organisms is due to the highly accumulated organochlorine residues in soil, and because of their resistance to biodegradation they succeed to contaminate vegetation, which makes the food of living organisms in the area. Another possible source of vegetation contamination could also be rainwater, which carries an uncountable number of organic and inorganic pollutants at trace level.

**CONCLUSIONS**

The presence of these chemicals in the eggs of the tortoises is very worrying or should be worrying, given the fact that these have been banned from use and production sometime in the mid 1970s. However, supposing Romania did not obey the rule until 1989, it is still worrying that we found such high concentration levels of these toxic chemicals. There are too many factors involved when trying to give an explanation why these eggs never hatched, and we cannot affirm that the only reason was the presence of these pesticides. But we can certainly say that this was an important factor that affected the normal juvenile development.

However, it is still necessary to continue the research, first of all to try and identify the level of pesticide concentration in eggs that have been incubated and normally hatched, and also analysis must be done on the specific species of plants that represent the tortoise diet. Some soil samples must be analysed in order to see if the normal trophic chain rules obey.

It is vitally important to state with a 100% certainty if the presence of the non–biodegradable residues has a major importance as far as the reproduction and growth of the *Testudo Hermanni Boetgeri* is concerned, as it is an endangered species whose development depends on the environmental conditions in its preferred habitats.

**ACKNOWLEDGMENTS**

Partial funding for this study was provided within the project LIFE Nature LIFE00/NAT/RO/7171 “Iron Gates Nature Park - Habitat Conservation and Management”. We
would like to thank the people who contributed to field sampling: Professor Maria Patroescu - coordinator of Life project, Viorel Popescu, Cristian Tetelea.

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PESTICIDES WATER CONTAMINATION IN BULGARIAN DANUBE REGION

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Galia Bardarska
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INTRODUCTION
Bulgaria has a well defined monitoring scheme for surface and groundwater quality which is upgraded yearly on the base of results of analysis. The Executive Environment Agency (EEA) in Sofia city executes the pesticides monitoring in the Bulgarian Danube region (EEA year book, 2002-2004). The length of Bulgarian part of Danube river is from km 845.5 to km 375.2. The catchment area is 46930 km² or 5.74% from total Danube catchment area (Figure 1).

Pesticides are normed according to Bulgarian Regulation No 7/ 1986 for water quality of surface waters. An example for pesticides groundwater pollution in drinking wells is mentioned in this paper as well.

MATERIALS AND METHODS
The monitoring program includes monthly analysis of Danube river water. Samples are taken by qualified specialists of Regional laboratory in Montana town and exported to the chromatography laboratory in EEA, equipped by PHARE. The number of monitored points are 3: right stream-near Bulgarian coast, left stream-near Romanian coast and middle stream-talveg.

In the chromatography laboratory in EEA are available Hewlett Packard 5890 series II Gas chromatograph with HP 5972 Series Mass Selective Detector (MSD) and Thermo Finnigan (TF) Trace GC/ Trace DSQ MSD. The both meth-
ods BDS EN ISO 6468:1996 and ISO 10695:2000, respectively for Organochlorine pesticides (OCP) and for Triazines (TRZ) include liquid-liquid extraction with organic solvent and GC/MS analysis. In total, 25 OCP and 7 TRZ are analyzed (Table 1). Only two of them (Aldrine and Atrazine) are normed according to Bulgarian Regulation No 7/1986.

**RESULTS AND DISCUSSION**

In 2002-2004 all water samples of Danube river (between Novo selo and Romanian coast) have lower Atrazine concentrations (0.003 - 0.129 $\mu$g/l) than Atrazine permitted rate of 250 $\mu$g/l (Table 2). Aldrin concentrations are under the detection limit of the method-0.002 $\mu$g/l (Table 2).

The pesticides concentrations have seasonal and spatial contribution. They are highest in Autumn. Middle stream has higher pesticides levels than right stream pesticides levels. It is clear noticed that pesticides concentration levels decrease during the years (Figures 2 and 3).

<table>
<thead>
<tr>
<th>Table 1: List of pesticides, monitored by EEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organochlorine pesticides/ BDS EN ISO 6468: 1996</td>
</tr>
<tr>
<td>$\alpha$,$\beta$,$\gamma$,$\delta$-HCH</td>
</tr>
<tr>
<td>Heptachlor</td>
</tr>
<tr>
<td>cis,trans-Heptachlor epoxide</td>
</tr>
<tr>
<td>Endosulfan II</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2: Pesticide concentrations of Danube river water in the period 2002-2004</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pesticide, $\mu$g/l</td>
</tr>
<tr>
<td>Simazine</td>
</tr>
<tr>
<td>Atrazine</td>
</tr>
<tr>
<td>Promazine</td>
</tr>
<tr>
<td>Prometryn</td>
</tr>
<tr>
<td>Terbutryn</td>
</tr>
<tr>
<td>Aldrin</td>
</tr>
<tr>
<td>*en = Romanian, r = right, bg = Bulgaria, la/breg = middle stream</td>
</tr>
</tbody>
</table>

Generally, the groundwater of Bulgarian Danube region is contaminated by Triazine pesticides (Atrazine, Propazine, Simazine) but its concentrations are under allowed rate. Local example for pesticides groundwater contamination was described in Bivolare research project (DEPA project No. 124/008-004, 1997-1998). The Bivolare well field is a part of drinking water supply system of Pleven town, center of Danube River Basin Directorate. The main parameters of Bivolare well field are as follows as:

- 29 wells with 3 m diameter and depth from 9 m to 12.5 m;
- 2 infiltration trenches (length of 2076 m and area of 21000 m²) for artificial groundwater recharge to the wells with Valtchovetz dam water;
- total water capacity of Bivolare well field - 360 m³/h without artificial groundwater recharge and 1620 m³/h with artificial groundwater recharge;
- 2 pumping stations and 2 water reservoirs with volume of 2000 m³ and 5500 m³ each.

Sometimes, uncontrolled agriculture activities impact Bivolare groundwater pollution with:

- Simazine 0.029 - 0.146 $\mu$g/l,
- Atrazine 0.011 – 0.048 $\mu$g/l,
- p,p-DDE 0.027 – 0.909 $\mu$g/l,
- p,p-DDD+p,p-DDT 0.022 – 0.054 $\mu$g/l,
- Methoxychlor 0.008 – 0.400 $\mu$g/l.

The comparative analysis between construction of new drinking water plant and drilling of deep wells showed deep water usage as an appropriate way to get over the pesticides water contamination. The task of two bore holes was looking for drinkable water in the Maestrictiam aquifer as an alternative for additional water supply to the Pleven region. The locations of both sites were defined by terrametric method (Figure 4).
CONCLUSIONS
The main conclusions for pesticides water contamination in Bulgarian part of Danube river are:
• Pesticides contamination of surface waters in Danube region is lower than Bulgarian norms;
• Lack of well defined sanitary-protected zones around drinking wells is a main reason for pesticides groundwater contamination over Bulgarians norms for drinking water in agricultural areas (Photo 1).

REFERENCES

EMISSION AND RESIDUE INVENTORIES FOR SELECTED ORGANOCHLORINE PESTICIDES AND THEIR CONTRIBUTIONS TO THE ENVIRONMENTAL STUDY

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Canada

ABSTRACT
During the last decade, a number of studies have been devoted to the sources and emissions of Persistent Organic Pollutants (POPs) on regional and global scales. A major portion of POPs is organochlorine pesticides (OCPs), in which carbon and chlorine are combined.

The high standard emission inventories for OCPs are considered a valuable contribution to the effort to understand and predict the distribution and fate of these chemicals. Since the early 1990s, Science and Technology Branch, Environment Canada started a serious studies to establish the emission inventories of OCPs in both global and regional scales, and to study the impact of these emissions to the environment worldwide, the Arctic in particular.

In the absence of complete data and information on worldwide inventories of pesticides emissions and residues, a Simplified Gridded Pesticide Emission and Residue Model (SGPERM) has been developed to estimate the emissions and residues, and build pesticide emissions and residues inventories. The SGPERM is an integration of a mathematical module, a relational database system, and a geographic information system. In this paper, a brief description of the model is given. The model is used to create global gridded emission inventories for α- and β-HCH, DDT, and endosulfan, and residue inventories of α-HCH with a1° latitude by 1° longitude resolution. Emission and residue inventories for selected OCPs have also been created for the United States, Canada, China, and the former Soviet Union on regional scales with a1/6° latitude by 1/4° longitude resolution. The contributions of these emission and residue inventories to the environmental research, especially to the Arctic study and the North American Great Lake’s study are presented.

1. INTRODUCTION
A pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest. Pests can be insects, mice and other animals, unwanted plants (weeds), fungi, or microorganisms like bacteria and viruses. By their very nature, most pesticides create some risk of harm to humans, animals, or the environment because they are designed to kill or otherwise adversely affect living organisms. At the same time, pesticides are useful to society because of their ability to kill potential disease-causing organisms and control insects, weeds, and other pests. Biologically-based pesticides, such as pheromones and microbial pesticides, are becoming increasingly popular and often are safer than traditional chemical pesticides. (http://pested.unl.edu/whatis.htm).

Persistent Organic Pollutants (POPs) is a common name giving to a group of pollutants that are semi-volatile, persistent, bioaccumulative, and toxic (e.g. Vallack et al. 1998; Jones and de Voogt, 1999). A large portion of POPs is the organochlorine insecticides (OCPs) in which carbon and chlorine are combined.

There is considerable evidence that POPs, including OCPs, circulate globally and accumulate in remote areas like the Arctic (Macdonald et al. 2000), and thus attracting international concern.
Several international agreements have been reached to reduce future environmental burdens of those POPs and heavy metals. One such agreement is the 1998 Aarhus Protocol on POPs under the 1979 Geneva Convention on Long-range Transboundary Air Pollution (LRTAP Convention) (UNECE, 1998). The overall and long-term goal of the Aarhus Protocol on POPs is to eliminate any discharges, emissions and losses of POPs to the environment. The Aarhus Protocol listed 16 POPs substances, 11 of which are organochlorine pesticides (OCPs). The 11 OCPs are aldrin, dieldrin, endrin, chlorpyrifos, DDT, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene, chlordecone, and lindane.

Another recent international agreement is the Stockholm Convention on POPs which is aimed at eliminating or at least controlling twelve POPs (aldrin, chlordane, dieldrin, DDT, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, PCBs, dioxins and furans) (UNEPE, 2002, 2003), 9 of which are OCPs, which are aldrin, dieldrin, endrin, chlordane, DDT, heptachlor, HCB, mirex, and toxaphene.

Knowledge about the sources and releases of POPs into the environment are therefore essential if these international agreements to be effective. The establishment of emission inventories for OCPs and other POPs is very important, not only because these emission inventories can provide the basis for further emission reductions by parties to the convention (e.g. UNEP, 1999, 2001; Vestreng and Klein, 2002), but they are also used by environmental scientists to understand the behavior of POPs and thus develop and predict source-receptor relationships for POPs at regional (e.g. Van Jaarsveld et al. 1997) and global scales (e.g. Li and Bidleman 2003; Li et al. 1998a, 2002; 2004a; Wania et al. 1999).

Since the early 1990s, Science and Technology Branch (STB) (Previous names: Atmospheric Environment of Canada (AES) and Meteorological Service of Canada (STB)), Environment Canada started a series of studies to establish the emission inventories of OCPs on both global and regional scales, and to study the impact of these emissions to the environment worldwide, the Arctic in particular. The efforts made by STB have significantly contributed to the Canadian Northern Contaminants Programme (NCP), the Arctic Monitoring and Assessment Programme (AMAP), a joint programme supported by eight Arctic countries, and the Global Emissions Inventory Activity (GEIA), a component of the International Global Atmospheric Chemistry (IGAC) core project of the International Geosphere-Biosphere Program (IGBP).

This paper provides a review of the research work with respect to the emission inventories of OCPs and their contribution to the environmental research global-wide, with focusing on the work carried at STB, Environment Canada. The Simplified Gridded Pesticide Emission and Residue Model (SGPERM), which has been used to develop the inventories for these OCPs, is introduced in Section 2. Section 3 is contributed to the discussion of the pesticide usage, emission, and residue inventories, and followed by the introduction of their contributions to the environmental research in Section 4. Section 5 presents our website GloPeRD (Global Pesticide Release Database).

2. SIMPLIFIED GRIDDED PESTICIDE EMISSION AND RESIDUE MODEL (SGPERM)

The SGPERM [Li et al. 2005b] has been designed for creating annual gridded emission and residue inventories on different scales. It consists of three major parts (steps): data acquisition, information allocation, and emission and residue calculation. In data acquisition, information for pesticides usage, application dates and modes of pesticide should be collected, usually based on political units (e.g. countries or provinces) or special regions. In information allocation, all information collected in the step of data acquisition should be digitized and allocated in a grid system, which is created according to the area covered by the study, by using GIS (Geographic Information System). All these gridded data are stored and managed within the database, and used in the third step to calculate the emissions and residues for each year within each grid cell through the use of a mathematical module. The synergy among these three parts is maintained by a control panel. The developed modeling system can simulate simultaneously pesticide emissions and residues. The estimates from the model are in turn entered into a database management system with the final results displayed and visualized through a GIS. The details of the model can be found in [Li et al. 2005b].

3. PESTICIDES USAGE, EMISSION, AND RESIDUE INVENTORIES

Since the early 1990s, Science and Technology Branch (STB), Environment of Canada has carried out a series of studies to establish the usage, emission, and residue inventories of OCPs on both global and regional scales, and to study the impact of these emissions and residues to the environment worldwide, the Arctic in particular. The major inventories created in STB are listed in Table 1, which are described in detail in the following subsections.

3.1. Gridded pesticide usage inventories

Figure 1 presents gridded toxaphene usage in the United States with 1/6° by 1/4° latitude /longitude resolution on croplands between 1947 and 1986. The intensive use of toxaphene on croplands was concentrated in the southeastern part of the United States with the largest usage of 2,070 t per cell. This area includes six states: Arkansas, Louisiana, Mississippi, Alabama, Georgia, and South Carolina. Use of toxaphene on livestock occurred in Texas, Missouri, Kansas, South Dakota, California, Iowa, Oklahoma, Nebraska, Kentucky, Wisconsin, Tennessee, and Minnesota. Usage inventories for other OCPs can be found in Table 1.

3.2. Gridded pesticide emission inventories

The global gridded emissions for α-HCH are presented with emissions due to the current use, due to residues of α-HCH used in the preceding 15 years, and due to both the current use and residues [Li et al. 2000b]. It shows that in 1990, 7 years after China banned the use of technical HCH in 1983 [Chinese Ministry of Agriculture, 1989], the residual α-HCH in Chinese soil still produced emissions to the atmosphere. Emission inventories for other OCPs can be found in Table 1.
3.3. Global pesticide residue inventories

Organochlorine pesticides are a major part of persistent organic pollutants, and can stay in soil for a long time after application. The residues of OCPs in soil can emit to air depending on climate conditions, soil type and other factors even the use of the pesticides is stopped. Hence, the residue inventories have to be compiled in order to improve the accuracy of the estimates of the emissions of these pesticides.

Inventories of pesticide residues in agricultural soil are also important for some models [Harner et al., 2001; Scholtz et al., 1997; 1998] to predict pesticide volatilization. Although direct measurements of soil samples in representative agricultural lands can be helpful in determining the reservoir of pesticides available for emission, they are labour intensive and costly.

Residues of toxaphene in cropland in the United States have been calculated between 1947 and 2004 according to equation (6). Gridded inventories, on a 1/4° longitude by 1/6° latitude resolution, of toxaphene residues in agricultural soil in the United States at the beginning of 2000 is shown in Figure 2. It is the first gridded inventories for pesticide residue. The results indicate that, almost 20 years after the ban of toxaphene use in the USA in 1982, the total toxaphene residues left in agricultural soil in the United States were around 29 kt, among which 360 t will be emitted in 2000 (Figure 3) (Li et al. 2001).

3.4. Uncertainty

It is difficult to verify the accuracy of pesticide emission data. Some other ways, however, could be used to check the quality of emission inventories indirectly. For example, high quality of usage data usually indicates high quality of emissions.
Based on the toxaphene residue inventories in the United States [Li et al. 2001], the average concentrations of toxaphene in agricultural soil can be calculated. Assuming that toxaphene was contained in the top 10 cm layer of soil and using a soil density of 2.65 g cm\(^{-3}\) [Cuenca, 1989], the average soil concentrations in each state of the USA in 1971 is determined from gridded toxaphene residue inventories in agricultural soil in the same year shown in Figure 4 (Li et al. 2001). These compare very well with data from a 1971 survey by the National Soils Monitoring Program (NSMP) and shown in Figure 5 [Carey et al., 1978a; b]. The comparisons in the southeastern parts of the United States are particularly noteworthy.

Figure 6 gives the trends of toxaphene residues in agricultural soil in one grid cell close to the city of Montgomery in the state of Alabama between 1950 and 2000 estimated from the toxaphene residue inventories. The measurements of soil concentrations of toxaphene in 1971 [Carey et al., 1978b] and 1996 [Harner et al., 1999] are also presented.

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Taihu Lake Basin is one of the most developed regions in China, which includes the city of Shanghai, parts of Jiangsu province and Zhejiang province, and was also one of the areas with the highest usage of technical HCH in China. Accumulated technical HCH usage between 1952 and 1984 on croplands in Taihu Lake Basin from our calculation is in good agreement with a survey in 1985 gave an average accumulated usage rate for technical HCH on cropland in the Taihu Lake Basin after 33 years of application of this insecticide since 1952 [Li et al. 2001].

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Study of the trends of \(\alpha\)-HCH residues in agricultural soil in Japan since 1950 shows that the trends of \(\alpha\)-HCH concentration in the soils estimated using our model fit the monitoring data in the same areas quite well [Li et al. 2005b].
4. CONTRIBUTIONS TO ENVIRONMENTAL RESEARCH

The establishments of OCP emission/residue inventories have contributed greatly to environmental research. These contributions include the study of sources and pathways of OCPs to the Arctic and the Great Lakes of the North America. These emission and residue inventories have also been used by modelling communities worldwide.

4.1. Sources and Pathways of OCPs to the Arctic

Figure 7 shows the long-term trends of global emissions of α-HCH and its mean air concentrations in the Arctic region from 1979 to 1996 [Li and Bidleman, 2002], which shows a high correlation between these two. The quick response of α-HCH concentration in the Arctic air to the change of global α-HCH emission shown in Figure 7 has given the strongest evidence that atmospheric long-range transport provides rapid dispersion of α-HCH from its source regions into the Arctic. The correlation is so strong that a reasonable estimate of historical air concentration of α-HCH in the Arctic can be inferred from its global emission data [see Figure 8, Li et al. 2004a].

Information for β-HCH suggests that it did not exhibit an even stronger predisposition to accumulate under the pack ice of the Arctic Ocean as might be inferred from an emission history similar to that of α-HCH and a Henry’s law constant twenty times lower. In contrast, β-HCH appears to have been less subject to direct atmospheric loadings into the high Arctic. Rather, it was rained out or partitioned into North Pacific surface water and subsequently entered the Arctic in ocean currents passing through Bering Strait [Li et al. 2002]. β-HCH provides an important lesson that environmental pathways must be comprehensively understood before attempting to predict the behavior of one chemical by extrapolation from a seemingly similar chemical [Li et al. 2002].

The divergence of α- and β-HCH pathways to the Arctic Ocean has produced a corresponding divergence in the temporal and spatial trends of their concentrations in the Arctic air and waters. Concentrations of α-HCH in the Arctic atmosphere are closely linked to global emissions before the early 1990s reaching as high as 900 pg/m³ in 1982. On the other hand, the atmosphere has not provided a very efficient transporting mechanism to deliver β-HCH to the Arctic Ocean from the source region, and β-HCH has arrived in the Arctic via ocean currents through Bering Strait with a considerable delay. The highest recorded concentration in arctic air for β-HCH was only ~1 pg/m³ in 1988. The restricted entry of β-HCH into the Arctic Ocean has resulted in far lower concentrations of around 0.2 ng/L or less for β-HCH within Arctic Ocean surface water in comparison to 7 ng/L and possibly higher for α-HCH and around 1.2 ng/L for b-HCH in the Bering-Chukchi region.

The temporal and spatial variations of α- and β-HCH in the Arctic air and waters are reflected in biota. Temporal trends of α-HCH concentrations in ringed seals from Arctic Bay, in beluga whales from Cumberland Sound, and in female polar bear from Hudson Bay indicate a decrease while, at the same time, the relative proportion of β-HCH is increasing. In eggs of thick-billed murres, concentrations of α-HCH and γ-HCH are significantly declining while β-HCH continues to increase. Whereas concentrations of α-HCH in ringed seals in the Arctic Ocean were higher than those in fur seals living in the Pacific Ocean, concentrations of b-HCH in ringed seals in the Arctic Ocean were lower than those in fur seals. Average concentration of β-HCH in human plasma from the Bering Strait and the Chukchi Sea was much higher than those observed for other native populations depending on marine mammals living in Greenland, Canada, and Faeroe Islands.

Bowhead whales have been shown to exhibit a reversal in their blubber α/β-HCH ratios as they migrate and feed annually along the path between the Bering to the Beaufort Sea. In contrast to other OCPs, concentrations of β-HCH in ringed seals tend to be higher in the Berinny-Chukchi Sea region than further east on a circumpolar basis. Concentrations of β-HCH in polar bears and Arctic fox from Barrow, Alaska, USA are also higher than those from Canadian Arctic. These trends and distributions can be simply related to ocean surface water trends in HCH concentrations [Li and MacDonald, 2005].
4.2. Trends of Great Lakes precipitation.

Figure 9 shows the global emissions of $\alpha$-HCH between 1980 and 1998 and the volume weighted mean concentration of $\alpha$-HCH in precipitation at Sibley, Ontario, Canada from 1985 to 1998. Global $\alpha$-HCH emissions peaked in 1980 and dropped significantly in the early 1980s. The dramatic decline in precipitation concentration at Sibley also happened in the 1980s, from 15-25 ng/L in the mid-eighties to 2-3 ng/L in the late nineties, coinciding well with the reduction in global emissions [Hites et al. 2002].

4.3. Global and regional modelling

In this sub-section, results from some models to simulate the transport of OCPs with our emission inventories as input are presented.

4.3.1. $\alpha$-HCH budget in the Arctic Ocean: The Arctic Mass Balance Box Model (AMBBM)

Constructing a mass balance for OCPs helps to develop an understanding of the processes controlling the input and fate of these OCPs as well as to identify knowledge gaps critical to prediction of future trends of these chemicals.

The Arctic Mass Balance Box Model [AMBBM, Li et al. 2004a] is created in the context of the Arctic as a receptor, and has three major components: the air concentration module, the water concentration module, and the transport/transformation module. The air concentration module calculates the historical air concentrations of $\alpha$-HCH in the Arctic (Figure 8) by using the global $\alpha$-HCH emission data [Li et al. 2000; Li and Bidleman, 2003]. The water concentration module calculates the historical water concentrations of $\alpha$-HCH at the Bering Sea, the Northern Atlantic Ocean, and the outlets of the major Russian rivers entering the Arctic Ocean. The monitoring data and interpolation techniques are used to compile the water concentrations of $\alpha$-HCH at the Bering Sea and the Northern Atlantic Ocean, and the residues of $\alpha$-HCH in Russian are used as the surrogate to estimate the water concentrations at the outlets of the major Russian rivers. The transport/transformation module calculates the loadings and removal of $\alpha$-HCH by gas exchange, degradation, and advection.

Figure 10 gives the estimated amount of $\alpha$-HCH loading to and removal from the Arctic waters between 1942 and 2000. It shows that gas exchange (49.3%) and sea current (35.6%) are the dominant pathways of $\alpha$-HCH entering the Arctic Ocean and sea current (40.9%) and microbial degradation (38.8%) are the dominant means for $\alpha$-HCH removed from the Arctic Ocean.

Figure 11 shows the loading to, removal from, and total burden of $\alpha$-HCH in the Arctic waters. It shows that (1) the amount of $\alpha$-HCH burden had accumulated since early 1940s and reached the highest value of 5000 t in the 1982, since then the burden of $\alpha$-HCH in the Arctic waters has decreased; (2) the burden of $\alpha$-HCH in the top 200 m water column of Arctic waters was 2900 t in 1990, which is close to the estimation of 2910 t for the early 1990s by Macdonald et al. (2000) [Li et al., 2004a]; (3) the amount of $\alpha$-HCH burden decreased in the 1990s by the annual rate of around 170 t/y; and (4) the complete elimination of $\alpha$-HCH from the Arctic waters could need another decade [Li et al. 2004a].

4.3.2. Budget and loading of $\gamma$-HCH over the Great Lakes Ecosystem

A coupled atmospheric transport, soil-air, water-air exchange model was developed to investigate the impacts of atmospheric transport and reemission on budget and loadings of $\gamma$-HCH to the Great Lakes [Ma et al. 2003] by using usage inventories of $\gamma$-HCH (Li et al. 2004b). Numeri-
5. GLOBAL PESTICIDE RELEASE DATABASE (GLOPERD)

Suitable gridded emissions inventories for pesticides are rarely available, especially on a global scale. The Global Pesticide Release Database (GloPeRD) effort is developing inventories for emissions and residues of pesticides, organochlorine pesticides (OCPs) in particular at the present time, on both global and regional scales. A grid system with 1° longitude by 1° latitude resolution is adopted for inventories on a global scale, which is the same as the one used by GEIA, and a grid system with 1/4° longitude by 1/6° latitude resolution is for inventories on a regional scale. These authoritative inventories will be updated periodically and, if adopted as standards by the atmospheric modeling community, will remove some of the uncertainty inherent in intermodel comparisons.

GloPeRD inventories are available free of charge from the Data Center at the STB, Environment Canada (http://www.msc.ec.gc.ca/data/gloperd/).

Emissions inventory activities at GloPeRD are still carrying on. More and more datasets will be available for environmental scientists. As emissions-related activities evolve, updating existing inventories will be a vital and challenging task. This updating will reflect changes in technology, regulation, and culture that influence the emissions to and concentrations of species in the atmosphere. For many parts of the world, especially the developing countries, current inventories are very poorly known, and the construction and maintenance of reliable inventories on appropriate spatial scales will be a major undertaking.

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DEVELOPMENT OF CONDITIONS, ISSUES AND CAPACITY BUILDING NEEDS IN THE PESTICIDES MANAGEMENT IN BULGARIA (The point of view of the NGO’s assessment)

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I. Seriousness of the problem towards the connected to the environment, human health and welfare: we are reporting our monitoring and efforts concerning to the capacity building needs in the pesticide storages, sites and following pollutions from them in Bulgaria on the base of the next two documents:

Marking the start of ambitious international efforts to rid the world of PCBs, dioxins and furans, and nine highly dangerous pesticides, and with the intention saving lives and to protect the natural environment – particularly in the poor communities and countries – by banning the production and use of some of the most toxic chemicals known to humankind.

Environmental Protection Act (Promulgated, State Gazette No. 91/25.09.2002 Corr., SG No. 96/2002)
“Article 3: Environmental protection is based on the following principles:
1. Sustainable development;
2. Prevention and reduction of risk to human health;
3. Priority of pollution prevention over subsequent elimination of pollution damage;
4. Public participation in and transparency of the decision making process regarding environmental protection;
5. Public awareness regarding the state of the environment;
6. Polluter pays for damage caused to the environment;
7. Conservation, development and protection of ecosystems and the biological diversity inherent therein;
8. Restoration and improvement of environmental quality in polluted and disturbed areas;
9. Prevention of pollution and damage and of other adverse impacts on clean areas;
10. Integration of environmental protection policy into the sectoral and regional economic and social development policies;
11. Access to justice in the environmental matters”.

According to the above papers and main principles at present the improvement of the environmental status in Bulgaria is a necessary condition to the social and economic revival. The activities of the authorities and NGOs in the field of the new environmental policy have to be related not only to the solution of the existing environmental issues, but to the prevention of new problems as well.

II. Historical Decision making in the field of the obsolete pesticides:
Having in mind the complexity of the problems, this calls for multi-planned actions. The decision making in the field of the obsolete pesticides management, including the hazardous chemicals in Bulgaria is an extremely difficult process, requiring specialized information concerning:
- the existing environmental and health risks,
- issue of the diversity of pollutants,
- Information on some specific factors operating in the country as well.

III. Point of view NGO’s assessment
More than 10 years problems and capacity building needs in the management of the banned, severely restricted and obsolete pesticides in Bulgaria staying and waiting for the “express decision”.

1) During that period the main actions of the authorities regarding to the pesticides’ problem in Bulgaria were:
The financial statement – three ministers: Minster of the Environment, Minister of Agriculture and Minster of the Health and General Nikolov – Civil Defense, announced their important statement for Necessity of expression of decision making to the Premier Minister Luben Berov, April’1994.
April’1995 – Report of the Minister of Environment to the deputy Premier Minister D. Konakchiev – “Allowing the issue of the obsolete pesticides in Bulgaria”.

2) The Correct Decision Making
After too many dangerous accidents all over the country, including conflagrations, burnings of unsafe stored sites, pollutions of large water bodies, etc., the authorities start particular processes of the pesticides’ collection in Bulgaria. September’ 1997 the correct decision of the Minister of the Environment to export and incinerate abroad 400 t pesticides.

3) The Conditions now
In the beginning of the democracy process in Bulgaria (1989) there are more than 1500 stores.
Many were destroyed, other replaced, but half (about 700) of the old pesticide stores are still there now. Most of them ~ 2/3 are not guarded and in very bad condition. In these stores there are DDT, lindane and many other POPs pesticides and those that are banned or restricted as well. The rest is unidentified or mixed with their damaged packages.

4) Public Participation in Decision-Making
During that period the NGOs assessment of the conditions and capacity building is needed in the obsolete pesticides management in Bulgaria, including the available data.
IV. Common Notices & Necessary Actions

- Responsible authorities must work out a list of former and existing stores of the pesticides.
- Most contaminated sites should be cleaned up in a way which will not lead to create new POPs or contaminated sites.
- Not appropriate stores could be replaced where such a safety practice can be started.
- More pesticides levels in the environment should be measured and more of them should be added to list of substances under the government decrees.
- Most likely no action is needed for the general levels of already banned old pesticides in the environment, but cleaning up the places contaminated by them can help.

V. Necessary Emergency Actions:

1) Citizens and NGOs must learn that they have rights.
- Information campaign about a right of free access to information with reference to the Arhus convention and/or the national legislation.
- Brandnaming of agencies which refuse to give information and/or ask for in inappropriate amounts of money.
- Involving journalists and the public media in educational activities on the process of getting access to information.
- Public hearings about state of obsolete pesticides.

2) Creating of Geospatial Informational System (GIS) in Bulgaria

Our efforts in the last years concerning the capacity building needs in the scope of obsolete pesticides and relate to them high risk for the human health having as the main goal creating an active ITN network – Geospatial Informational System (GIS) on the Balkan Peninsula for a good cooperation with CENTRAL EUROPEAN and EECCA countries

VI. Proposals for Decision Making of the 8-th INTERNATIONAL HCH AND PESTICIDES FORUM FOR CENTRAL EUROPEAN and EECCA COUNTRIES

- Creating an active ITN network – Geospatial Informational System (GIS) for management and monitoring the storages, polluted by pesticides sites in regions on the Balkan Peninsula, and for a good cooperation with Central European and EECCA countries
- Bulgaria should be assigned as FOCAL POINT of the Obsolete Pesticides Program for the above countries, due to its good geospatial position.

OBsolete AND BANNED PESTICIDES IN UKRAINE:
CURRENT STATE, RELATED PROBLEMS AND ROLE OF EDUCATION

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Obsolete and banned pesticides are a separate group of highly toxic waste that poses high risk to human health and to the environment.

Pesticide toxic waste can be divided in three groups:

1. Banned pesticides
2. Obsolete pesticides mainly due to the term of validity and guaranteed shelf life, and as a result of deterioration when the condition of storage and transportation are inappropriate.
3. Unknown pesticides due to loss of labeling or mixed pesticides when it is not possible to identify the composition.

The legal and regulatory mechanism for obsolete pesticide management is provided in the framework of some International Agreements and Laws. Among them the Stockholm Convention on persistent organic pollutants and Rotterdam Convention on prior informed consent procedure for Certain Hazardous chemicals and pesticides in international trade, are the two most important ones.

STOCKHOLM CONVENTION [1]
Persistent Organic Pollutants (POPs) is a group of chemicals persisting in the environment a long time before they brake down, travel for a long distance to all parts of the globe, accumulate in the tissues and poise human and wildlife, causing a wide range of toxic effects. POPs may have serious effect on human health and increase the risk of birth defects and children mortality [1]. The fact is that POPs concentrate in the body due to the biological accumulation. Since these chemicals are not dissolved in the water, they adsorb in fatty tissue, quickly. Their concentration in fatty tissue reaches up to 70,000 times the background level. Since fish, predatory birds, mammals and human bodies consti-
tute the food chain, the value of POPs absorbed in human body which is on the top of the food chain may reach the critical level.

In case human and animals change their habitats, POPs migrate along with them even to remote areas thousands of kilometers from the nearest POPs source.

Presence of POPs has been documented in areas where they have never been manufactured and used. Because of the POPs negative impact on the global state of the Environment it is necessary to take some global actions on elimination of risk related to it. One of the relevant accomplishments was the adoption of Stockholm (POPs) Convention.

The Convention was adopted in Stockholm (Sweden) in 2001. Twelve POPs the so called “dirty dozen”, including pesticides, industrial chemicals and unintended byproducts are internationally recognized as needing immediate global action. These are the following.

Pesticides
- Aldrin
- Chlordane
- DDT
- Dieldrin
- Endrin
- Heptachlor
- Mirex
- Toxaphene

Industrial chemicals
- Hexachlorobenzene
(also a pesticide)
- PCBs (polichlorinated biphenyls)

Unintended byproducts
- Dioxins
- Furans

Banning the majority of the POPs should be done immediately after the Convention will take effect. The exception is DDT which is allowed to be used in the developing countries until the chemicals with the same type of action and non harmful for the environment will be discovered. This exception was made because of the wide use of this chemical to control mosquitoes. It is known [1] that control of malaria transmitted by mosquitoes is one of the core components on health guaranty in the development countries.

The Stockholm Convention deals also with polychlorinated biphenyls. Those chemicals are not produced industrially anymore, but hundreds of thousand tones of polychlorinated biphenyls are still being used in electric transformers and in other equipment.

In accordance to the Convention polychlorinated biphenyls can be used till 2025, providing for requested precaution measures. The task to find another chemical which doesn’t content PCBs should be solved till that time. The Convention points out the control measures on manufacturing, import, export and use of POPs and provision of effective technologies to replace existing POPs along with precaution measures dealing with impossibility to use new POPs.

National Legislation and Action Plans on Convention implementation are stipulated by its ratification

**ROTTERDAM CONVENTION [2]**

The Convention is known as the Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides on International Trade. The appearance of the Convention was caused by the fact that developed countries continue to transport compounds or compounds which use is severely restricted or banned in their own country, to developing countries.

Nowadays, there are up to 2 million different chemicals, including pesticides globally. The chemical industry takes the second place after motor- car industry on global sales, which makes up to 1.6 trillions USD. Global Chemicals Trade values around 480.000 million [2]. Therefore, the monitoring and control of import of the toxic hazardous compounds into the developing countries which is a Rotterdam Convention objective is timely.

The Convention was signed in Rotterdam (Netherlands) in September 1998. In November 2003, the Convention was ratified by 50th country which is Armenia and according to the procedure the Convention came in force on February 24, 2004.

The Convention implements using “PIC procedure”. It provides for joint response of countries that import and export the hazardous chemicals and pesticides.

Based on the Convention, countries importing hazardous chemicals are allowed to determine which chemicals should be imported further and which should not be imported because of impossibility to manage them effectively and safety. The Convention stipulates the exporting countries to follow the wishes of importing countries as well as mandatory labeling the imported chemicals and providing the importing countries with information on chemicals posing potential risk for public health and the environment.

There are 27 chemicals designated by Convention as hazardous ones, trade of those is banned globally or severely restricted 22 chemicals have been listed when the Convention was signed.

Aldrin, Captafol, Chlordane, Chlordimeform, Chlorobenzilate, DDT, Dieldrin, Dinoseb and dinoseb salts, 1,2-Dibromoethane, Fluoroacetamide, HCH (mixed isomers), Heptachlor, Hexachlorobenzene, Lindane, Mercury compounds including Pentachlorophenol, 2,4,5-T, Methyl-parathion, Parathion, Phosphamidon.

Some industrially manufacturing compounds are also listed: Crocidolite, Polybrominated biphenyls, Polychlorinated biphenyls (PCB), Polychlorinated terphenyls (PCT), Tris (2,3-dibromopropyl) and Phosphates.

Additional 5 hazardous compounds: Toxaphene, Ethylene dichloride, Ethylene oxide, Binapacryl and Monocrotophos were included in September 1998

**Obsolete Pesticides stockpiling reasons and current state in Ukraine**

The considerable quantities of obsolete and banned pesticides have been accumulated in the Ukraine and other NIS and Eastern European countries in 70s–80s of the last century when intensive technologies widely used in agriculture and the pesticide use ratio reached 3-4 kg/ha of arable land. The majority of pesticides used in that time became banned
afterwards. In that time, pesticide produced in the local plants or imported which could not be used were stockpiled in the agricultural areas. Another substantial part of the pesticide waste has been accumulated because of centrally managed and sometimes uncritical use of pesticides. The pesticide demand and supply regulated based on the Central Plan and leftovers of pesticides have been stored in collective and state farmers’ stockpiles for a long time, which caused the deterioration of their mode of action. As a result, obsolete and banned pesticides have been stockpiled in a large amount at the Central Stoppages operated under the State Union “Ukragrochim” or in the small storage where they were temporarily stored before use.

Due to the economic instability the ratio of pesticides use has decreased significantly and currently is approaching 0.7-1 kg/ha of arable land. During the 90s the ownership of stockpiles have changed several times. It resulted at the loss of labels and documentation, free access to the pesticide waste for unauthorized people and their illegal use. During the long term storage and loss of labels pesticides were mixed and the chemical reaction may have occurred. The low quality of containers and packaging materials has caused their destruction and contamination of sites surrounding the stockpiles and storage. At the territories attaching to these storage sites, buildings have been constructed that posed the risk to human health and to the environment. The situation has become even more complicated because the Governmental Authority lost their control functions of consumption of the imported pesticides as consequences of disappearance of State Agrochemical Service. Several chemicals, from which a large number revealed to be obsolete, were imported to the country at the beginning of 90s. It increased the volume of pesticide toxic waste. The total toxic pesticide waste in 1998 is presented in Table 1 [3-5].

As shown in the Table banned pesticides constitute 30% of the total amount as well as obsolete and unknown pesticides and mixed pesticides make up 20% and 50% correspondingly. Description of pesticide wastes by chemical classes is presented in Table 2. As shown in the Table up to 90% of pesticide waste belongs to the 1st-3 class, among those the largest amounts are chlorine containing compounds.

Ukraine carried out the preliminary inventory in 2000-2002. Interregional Pesticide Center data indicate that 8.5 thousand tons stored are documented in 147 Centralizes stores; 7 thousand tons are found in 5 thousand small poor quality storages, whereas 20% of those amounts are stored outdoors and 30% of stores are almost destroyed. Stores are found in each region of Ukraine. The largest single amounts of 1.1 thousand tons are found in Shavgorodsliy county of Vinnitska region and 450 tons in Novodoldzansky county in Chkarkivska region.

The Ministry of Ecology and Natural Resources convincingly indicates that in the year 2003, the total amount of obsolete and banned pesticides was as high as up to 20,000 tons? In 2005 this amount increased to 29,000 tons.

**Obsolete and banned pesticides management**

Pesticide use in agriculture is regulated by State Laws, Resolutions of Ukrainian Parliament Cabinet of Ministry and several Orders of the Ministry of Ecology Arraign Policy and Human Health Defense. The most important are the following documents:

- The Law on Pesticides and Agrochemicals (1966)
- The Law on State Program on Toxic Waste management (2000)
- The Law on Environmental Protection (1991)

The Law on Pesticides and Agrochemical deals with State Monitoring, issuing permissions for effective management of existing or new pesticides. Only Article 15 tattled “Removing, utilization and decontamination banned and obsolete” deals with pesticide waste and says that “banned or obsolete pesticides and agrochemical, containers should be removed, utilized, destroyed and decontaminated according with the established by Cabinet of Minister order”. To implement this proposition was adopted the resolution of Cabinet of Ministry No 354 “About endorsement of Order on removing, utilization, destroying and decontamination of banned and obsolete pesticides” issued in March 27, 1996.

The article 55 of Law on Land Protection of Ukraine makes provision for the Measures on utilization and decontamination of unknown and obsolete chemical compounds at the expense of State Budget of Ukraine.

Division 1 of Law on State program on Toxic Waste management describes banned chemical crop protection prod-

![](https://table.png)

Table 1: Amount of obsolete and banned pesticides in Ukraine

<table>
<thead>
<tr>
<th>Pesticides in facility</th>
<th>Total quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Banned pesticides</td>
<td>58</td>
</tr>
<tr>
<td>Obsolete pesticides</td>
<td>165</td>
</tr>
<tr>
<td>Unknown</td>
<td>-</td>
</tr>
</tbody>
</table>

| Number of chemicals   | 3428          |
| Weight in tonnes      | 1509          |
| 10132 (including 1550 buried) | 15.069 |

Table 2 [3]: Description of high toxic waste by active ingredients

<table>
<thead>
<tr>
<th>High-toxic pesticide waste</th>
<th>Banned pesticides</th>
<th>Obsolete pesticides</th>
</tr>
</thead>
<tbody>
<tr>
<td>tons</td>
<td>%</td>
<td>Tons</td>
</tr>
<tr>
<td>1. Chlorine containing</td>
<td>2700</td>
<td>79.0</td>
</tr>
<tr>
<td>2. Mercury containing</td>
<td>238.0</td>
<td>6.9</td>
</tr>
<tr>
<td>3. Sulphur containing</td>
<td>237.8</td>
<td>6.9</td>
</tr>
<tr>
<td>4. Arsenic containing</td>
<td>70.0</td>
<td>2.0</td>
</tr>
<tr>
<td>5. Nitrogen containing</td>
<td>45.6</td>
<td>1.3</td>
</tr>
<tr>
<td>6. Phosphor containing</td>
<td>30.9</td>
<td>0.9</td>
</tr>
<tr>
<td>7. Cyanide containing</td>
<td>27.7</td>
<td>0.8</td>
</tr>
<tr>
<td>8. Sulphur and nitrogen containing</td>
<td>5.7</td>
<td>0.2</td>
</tr>
<tr>
<td>9. Other</td>
<td>74.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Total</td>
<td>3428</td>
<td>100</td>
</tr>
</tbody>
</table>
ucts as “the separate group of Toxic waste”. The Law makes a provision for consequent reduction off all Toxic waste by mean utilization, decontamination and removing.

Division 3, paragraph 2 deals with immediate tasks for State Program on implementation, including the measures related to pesticide waste: “setting up and carry out register sites of accumulation, utilization and removing the toxic waste” and “development of basic technologies projects and equipment requested for toxic waste management”, “identify measures on decontamination of waste in storage sites”.

Division 3, paragraph 3 deals with stages on implementation intermediate (meddle term) steps should taken till 2005, including “utilization and removing obsolete chemical plant protection products which are stockpiled in stores”, “inspection and selection of sites for a long- term storing and burring the toxic waste” and carry out measures on cleaning up the contaminated areas”.

Monitoring of obsolete pesticides have been under competency of State department of “Uktragrochom” up to the 1998. After the liquidation of this organization its functions have passed to the State Soil Monitoring and Plant Protection Service Ministry of Agrarian Policy. Elimination of negative impact from the obsolete pesticides on the environment and Ukrainian population is in competence of Department of Waste Management within the Ministry of and their local branches as well as a special Union which is Interagency Environment Centre. State Department of Chemical Safety Management has a control functions. Interdepartmental Scientific- Regional Council co-ordinates of carrying out the State Program on Toxic Waste Management.

However, lack of the clear legislative-regulatory framework, the appropriate infrastructure, financial resources and active participation of civil society, Obsolete Pesticides Management, is still poor and obsolete pesticide stockpiles continue to expose the risk to human health in most regions of Ukraine.

To fulfil mentioned above gaps, the Project National Action Plan on elimination of risk from accumulation of Obsolete Pesticides was developed in 2000-2002.

Goal:
Elimination of stockpiled obsolete pesticides and related risk on human health and the environment.

Objectives:
– To identify the main directions in Obsolete Pesticides Management;
– To develop organisational, economical, technical measures to improve the legislative framework of safe obsolete pesticides management;
– To develop measures aimed at the Obsolete pesticides amount reduction;
– To create conditions for safe cleaning up and rehabilitation of sets contaminated by obsolete pesticides;
– To carry out measures aimed at the environmental awareness of local population;
– To raise awareness of local legislative and executive authorities on Obsolete pesticides related problems;
– To strength of the capacity involving in Obsolete Pesticides management institutions;
– To strengthen the co-operation between Governmental institutions and NGOs (general public, representatives of agricultural entities).

DISPOSAL OPTIONS FOR OBSOLETE PESTICIDES DESTRUCTION
There are several disposal options for obsolete pesticides as applicable under condition of the country:
– Burying in a especially designed storage
– Safe storage as a temporary measure for minimization
– Immobilization of pesticides waste
– Destruction by means of physical or chemical treatment.

1. Burying in a specially designed storage
Burying is carried out at special landfills. The landfill has a specially designed trench insulated with concrete slabs. The use of this option requires the strict following of the sanitary and ecological rules. There are strong measures demanded for packaging materials. This option also requires the removal of quite large land areas and presence of full time workers to monitor the state of the environment and to guard the works. Because of those reasons, this option is globally not used.

2. Temporary safe storage
This option includes the following:
– Inventory and database establishment.
– Select the site for temporary safe storage and supply it in accordance with the international standards.
– Repackaging of pesticide in long term containers (drums). Containers should be made from plastic or concrete, hermetically closed and labeled. Repackaging is done by workers specially trained in repackaging, transport and storage of obsolete pesticides and who have received the necessary certificate
– Transport of repackaging pesticides in containers to the centralized storage sites.

With the support of the Danish – Ukrainian Project (DANCEE) “Elimination of risk from obsolete and banned pesticides in Lozovoe Charkivska region” the storage site for temporary store of pesticides was set up and 150 tons were repackaged in plastic and metal containers in 2002.

3. Immobilization of pesticide waste
In this option pesticide waste is used in the production of building materials such as concrete, ceramic and asphalt. If pesticide waste is added to the asphalt for road construction, it is used as a backfill material which is then covered by a layer of the asphalt free of pesticide waste. Similarly, it is possible to add concrete, concrete slabs. The pesticide waste is then covered by a layer of “clean” concrete.

4. Physical or chemical treatment

4.1. Incineration
Incineration is the most feasible technology for destruction of obsolete pesticides. A list of conditions based on which waste should be incinerated is found in the recommendations of Royal Commission on environmental Protection [3]:
– if waste cannot be degraded biologically and stable in the environment;
- if waste cannot be used for recycling;
- if waste cannot distract using environmental sound options;
- if waste content of organically combined halogens of nitrogen, phosphor and sulphur.

Obsolete pesticide is fully matched with those requirements; therefore, their incineration is a feasible option of destruction. Cement kiln or rocket fuel incineration are used for the incineration. Cement kiln is found as an ecologically friendly option for pesticide destruction. [3], which results from the following:
- high burning temperature of clinker (up 1450 °C) and gas media (up 2000 °C);
- considerable residence time of waste at high temperature, for more than 7 seconds at temperatures up to 1200 °C;
- alkalinity of clinker in kiln with conditions of acid property of gases created during the process of incineration;
- transmission of clinker and gases in opposite flow and providing intensive contact between hard and gas phases;
- toxic metals neutralization due to the liquid phase of clinker;
- presence of appropriate electro-filters in kilns.

Organochlorine pesticides wastes may have undergone the complete destruction in industrial incinerators. In Ukraine this option has not widely been used due to economic instability and the absence of appropriate pesticide management.

Research was carried out and reported on the Cement Plant in Kamianets-Podilskij [3] at the beginning of 80s and indicated that 10 tons of pesticide waste have been co-incinerated. Obtained results were used for the creation of “Temporary guidelines for test burns of obsolete and banned pesticides in industrial kilns in Kamianets-Podilskij Cement Plant. The drawback of this incineration option is transportation of hazardous wastes from many storage sites, which causes additional expenses and additional requirements.

4.2. Pyrolysis

Carry out using mobile hydrolysis incinerators [6], which use directly in the waste pesticide storage sites.

The process consists of two stages” alkaline hydrolysis and low temperature hydrolysis. At the first stage wastes is mixed with solid caustic and with the solution of caustic soda and heated up to the 200-250 °C in a hermetic steel reactor. At the second stage temperatures should be raised up to 500 °C and hydrolysis is carried out till the gas emission finishes.

The solid residues do not contain hazardous organic compounds and may be buried. Advantage of this option is pesticides waste utilization in storage sites directly and absence of dioxins which may have been formed in case of incineration by high temperature.

Pyrolysis was used on Shostka (Sumska region) for utilization of 100 tones of pesticides wastes.

4.3. Alkaline hydrolysis

This option is useful to decrease of toxicity of some species phosphorus containing pesticides and also for carbonates. Hydrolysis is carried out in alkaline media obtaining hydrolysis products that are less toxic than initial compounds.

4.4. Biodegradation

This method is used to destroy some of pesticide waste by anaerobe bioreactors. The mixture content of pasture waste such as organic wastes as straw, leaves litter and residues of nitrogen, phosphorous and potassium fertilizers are put into the reactor made from concrete. The optimal conditions of a biodegradation process, such as humidity, pH, concentration of mineral nitration is determined experimentally in advance.

Table 3 presents the data on biodegradation of some pesticides [3].

4.5. Phytoremediation

Phytoremediation is used for cleaning up the soil from contamination caused by heavy metals, radionuclides, organic compounds and pesticides. This method is based on the property of green plants to stabilize, mobilize, extract or absorb different types of pollutants or their fragments in the soil.

This method is useful because green plants adsorb pollutants in quite a large concentration (up to 4 % of dry mass) accumulating 200-1000 kg of pollutants per 1 ha of contaminated soil annually.

These methods have a relatively small practical use, mostly in the US, Canada and Western Europe [7].

The role of education in effective pesticide management

The important components of obsolete pesticide management are the education and research, public awareness raising and active participation of citizens.

Obsolete pesticides managers around the world focus their work on the development and are providing the special training for public and for technicians who may have been working on utilization of obsolete pesticides and decontamination of polluted storage sites.

The are several Non-Governmental local and International Organizations, such as PAN-Europe, PAN-USA, Pesticides Forum, Women for Sustainable Future involved in education and public awareness for elimination of obsolete pesticide related risk. To draw the attention and join efforts of International Community and Governments of countries facing obsolete pesticide related problems is very important. Public meetings, conferences, seminars and forums may be very useful in order achieve it and should be carried out regularly.

International HCH and Pesticides Forum

The 7th International HCH and Pesticides Forum was held the first time in NIS in Kiyv on 5-7 June 2003.
ABSTRACT
A number of samples from Baltic herrings (Clupea harengus) were studied in 1994–2004 to investigate the content of HCH-isomers and their distribution in the fish of the Estonian waters of the Baltic Sea. The monitoring emphasis is placed on marine biota. The samples were taken in three areas of the Estonian coastal sea, two sites in the Gulf of Finland and one site in the Gulf of Riga, and analysed for the content of α-HCH and γ-HCH. On average, concentrations of γ-HCH (lindane) are higher by half than concentrations of α-HCH in the muscle tissue of Baltic herring. Concentrations of both compounds were lower in 2004 than in 2003. Elevated concentrations in 2001 may be caused by sampling Baltic herring older than three years.

Higher concentration of HCH-isomers, in particular lindane, was likely influenced by an increased content of these compounds in the environment. In 2004, concentrations of α-HCH and γ-HCH in the muscle tissue of Baltic herring were approximately on the same level in all sampled Estonian marine areas in the Baltic Sea. In 1994–1995, concentrations of α-HCH were the highest in the Gulf of Riga and, in contrary, the lowest in the Gulf of Finland near Kunda. An average concentration of α-HCH and γ-HCH varies between 0.006–0.030 and 0.008–0.034 mg/g lipids in the Baltic Sea as a whole. In summary, the concentration of HCH-isomers of sampled organisms in the Baltic Sea has levelled since late 1990s, however slightly elevated concentrations of lindane have been observed in some years. The concentration of α-HCH was likely influenced by an increased content of these compounds in the environment.

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4. Law of Ukraine on Pesticides and Agrochemicals, 1995
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DISTRIBUTION OF HCH-ISOMERS IN THE BALTIC HERRING OF THE ESTONIAN COASTAL SEA

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INTRODUCTION
By the World Health Organization (WHO), monitoring of persistent organic pollutants in animal-derived food, especially fish, should be carried out worldwide to determine the possible
sources of these contaminants in the diet. Since 1994, the analyses of hazardous substances originating from Baltic fish are part of the Estonian National Environmental Monitoring Programme. The aim of these investigations was to pinpoint the areas with higher toxicant concentrations, so that we could focus on the examination of these above-mentioned areas.

**MATERIAL AND METHODS**

The sampling time and location, i.e. the population location, play an important role when different areas are compared. In the period 1994–2004 HCH-isomer concentrations in the Baltic Sea fish from three areas of the Estonian coastal waters were determined.

We selected the Baltic herring (*Clupea harengus*), because:
- they can be caught in all parts of the Baltic Sea;
- they are an important commercial species;
- their biology and ecology is fairly well known;
- they are of suitable size for preanalytical sample treatment;
- they are easy to collect.

Fish were caught from the eastern (Kunda) and central (Tallinn) parts of the Gulf of Finland and Gulf of Riga (Liivi). The fish samples were frozen promptly following examination and selection. All organochlorine contaminants have been analyzed in the muscle tissue.

The Estonian Environmental Research Centre (EERC) is accredited by the German accreditation bureau Deutsches Akkreditierungs System Prüfwesen GmbH (DAP) (DAP-PL-3131.00 (2008-11-22). All solvents used were of the highest quality commercially available. Ten grams of the fish sample (muscle) were homogenized in an IKA T25 homogenizer from Labassco AB, Pertolle, Sweden and extracted according to Jensen et al.1 nd the lipid content was determined by the method in Roots et. al.2-3 solved lipid (0.1–0.2 g fat) extracts were cleaned up by method — a silica gel column treated with concentrated sulphuric acid. HCH-isomers were analysed on a 90 m capillary column (DB-5) using gas-chromatography (Varian 3380) with electron capture detector (ECD)[2-4].

**RESULTS AND DISCUSSION**

On average, concentrations of γ-HCH (lindane) are higher by half than concentrations of α-HCH in the muscle tissue of Baltic herring (Table 1).

![Figure 1: Concentrations of α-HCH in the muscle tissue of Baltic herring 1994–2004](image1)

![Figure 2: Concentrations of γ-HCH in the muscle tissue of Baltic herring (1994–2004)](image2)

![Figure 3: Concentrations of α-HCH in the muscle tissue of Baltic herring in various marine areas of the Estonian coastal Baltic Sea (Liivi = Gulf of Riga)](image3)

![Figure 4: Concentrations of γ-HCH in the muscle tissue of Baltic herring in various marine areas of the Estonian coastal Baltic Sea (Liivi = Gulf of Riga)](image4)

Concentrations of both compounds were lower in 2004 than in 2003. Concentrations of α-HCH and γ-HCH in the muscle tissue of Baltic herring were substantially elevated in the period 1994–1995 (Fig. 1–4).

To a certain extent, concentrations of HCH isomers were higher than average in 2001 and 2003. Elevated concentrations in 2001 may be caused by sampling the Baltic herring older than three years. Higher concentration of HCH isomers, in particular lindane, was likely influenced by increased content of these compounds in the environment. In 2004, concentrations of α-HCH and γ-HCH in the muscle

<table>
<thead>
<tr>
<th>Marine area</th>
<th>Period</th>
<th>Number of samples</th>
<th>-HCH</th>
<th>-HCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gulf of Riga (Liivi)</td>
<td>1994–1995</td>
<td>7</td>
<td>0.066</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>1996–2003*</td>
<td>11</td>
<td>0.008</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>2003</td>
<td>10</td>
<td>0.007</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>2004</td>
<td>10</td>
<td>0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>Tallinn</td>
<td>1994–1995</td>
<td>9</td>
<td>0.037</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>1996–2003*</td>
<td>11</td>
<td>0.008</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>2003</td>
<td>10</td>
<td>0.009</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>2004</td>
<td>10</td>
<td>0.005</td>
<td>0.000</td>
</tr>
<tr>
<td>Kunda</td>
<td>1994–1995</td>
<td>6</td>
<td>0.015</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>1996–2003*</td>
<td>8</td>
<td>0.010</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>2003</td>
<td>10</td>
<td>0.009</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>2004</td>
<td>10</td>
<td>0.004</td>
<td>0.001</td>
</tr>
</tbody>
</table>

* except 2001

106
tissue of Baltic herring were approximately on the same level in all sampled marine areas (Table 1). In 1994–1995, concentrations of α-HCH were the highest in the Gulf of Riga and, in contrary, the lowest in the Gulf of Finland near Kunda.

Differences in toxicant concentrations in perch living in different areas of the coastal sea could also be observed (Figs. 2 and 4). Samples from other years show similar concentrations of α-HCH in the muscle tissue of Baltic herring in all coastal sea areas (Fig. 1).

The concentration of lindane (γ-HCH) in the muscle tissue of Baltic herring is the same in all survey periods in the Gulf of Riga and in the Gulf of Finland (Fig. 4). An average concentration of α-HCH and γ-HCH varies between 0.006–0.030 and 0.008–0.034 mg/g lipids in the Baltic Sea as a whole. Ignoring data from the period 1994–1995, the concentration of lindane in the muscle tissue of Baltic herring is near the upper limit only in the area of Kunda (Table 1).

In summary, the concentration of HCH isomers of sampled organisms in the Baltic Sea has decreased considerably since the early 1980s up to 1998. It has been proved by this survey that the concentrations of HCH have staid constant since the late 1990s. However, elevated concentrations of lindane have been noticed in some years. Internationally, elevated levels of hazardous substances are associated with the western parts of the Estonian coastal sea, where the concentrations of hazardous substances are elevated due to long-range transportation of air pollution from Central and Western Europe.

REFERENCES

LINDANE IN THE BALTIC FISH IN THE ESTONIAN COAST OF THE BALTIC SEA

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INTRODUCTION
Evaluation of bio-accumulation of toxic compounds into the organism of fish from Estonian coastal waters depending on their age, sex, maturity of gonads and fishing ground. 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 other Baltic Sea countries and also with established standard norms, which will enable us to clarify how dangerous are the toxic compounds in fish to the human health. Thus the practical results will have an essential place alongside of the purely scientific objectives of the project.

Perch is one of the most abundant fish species in Estonian waters. The Estonian total annual catch (from the Baltic Sea) in the years 1994–1997 was from 300-600t, but shows a decreasing trend [1]. The concentration of lindane in perch of different areas of Estonian coastal sea has been studied since 1998. Differences in lindane concentrations in perch living in different areas (different catches) of the coastal sea could be observed.

MATERIAL AND METHODS

Materials
The main coastal fishing areas are Matsalu Bay, the Väinameri (Moonsund) Archipelago, and Pärnu Bay in the Gulf of Riga. In the period 1998–2003 HCH-isomers concentrations in the Baltic Sea fish from five areas of the Estonian coastal waters were determined. Fish were caught from the western (Dirhami) and eastern (Narva) parts of the Gulf of Finland, Pärnu Bay, Open part of the Baltic Sea (Vilsandi) and the Väinameri (Moonsund) Archipelago. The fish samples were frozen promptly following examination and selection. All organochlorine contaminants have been analyzed in the muscle tissue.

Methods
The Estonian Environmental Research Centre (EERC) is accredited by the German accreditation bureau Deutsches Akkreditierungs-system Prüfwesen GmbH (DAP) ( DAP-PL-3131.00 (2008-11-22). All solvents used were of the highest quality commercially available. Ten grams of the fish sample (muscle) were homogenized in an IKA T25 homogenizer from Labassco AB, Pertille, Sweden and extracted according to Jensen et al. [2] and the lipid content was determined by the method in Roots et. al [3-4]. Dissolved lipid (0.1-0.2 g fat) extracts were cleaned up by method – a silica gel column treated with concentrated sulphuric acid. HCH-isomers were analysed on a 90 m capillary column (DB-5) using gas-chromatography (Varian 3380) with electron capture detector (ECD)[3-4].

RESULTS AND DISCUSSION
Before beginning an ecological parameters investigation, each scientist must select what kind of biological param-
eters to measure in order to measure all the essential parameters simultaneously. The need for adequate fish sampling and biological parameters analyses in ecotoxicological investigations is demonstrated in our earlier work [5].

In Estonia the contents of persistent organic pollutants (POPs) [6] in ecological system of the Baltic Sea have been researched since 1974. In the first period (1974-1991), the aim of the research project was to investigate the mechanisms that determine how organochlorines spread and move around in the environment. Findings on deposition and the concentrations in air and precipitation all over the Baltic Sea (Table 1) will be combined with studies of atmospheric transport, seawater processes and cycling between water, plankton, fish algae, molluscs, seals, etc. The data have shown that many organochlorine substances which have never been used in Estonia have been carried to the Estonian coast by air or surface currents.

Preliminary investigations described the results of large-scale environmental monitoring of the hazardous substances in Estonian coastal water ecosystems. At the beginning of nineties it became evident that every catch (or fish population) of fish (Baltic herring) is unique, so the parameters of different catches (or populations) cannot be described as a single array [8].

Statistical analysis. Instead of measured fish quantities $X_i$ as length [mm], weight [g], age [year], maturity, and lindane [microgram/kg] we use modified values $X_i'$, where

$$X_i' = (X_i - \text{average } X_i)/\text{standard deviation } X_i.$$

Using Monte-Carlo method are searched for set of constants $C_i$ in linear form

$$Z = C_{\text{length}} \times \text{length}' + C_{\text{weight}} \times \text{weight}' + C_{\text{age}} \times \text{age}' + C_{\text{maturity}} \times \text{maturity}$$

prerequisite linear correlation constant $R$ to be maximum between $Z$ and lindane. Supplementary condition is maximum stability of $R$ regarding to changes of constants $C_i$. On that conditions we can interpret values of $C_i$ as relative importance for factors $i$ in establishing lindane values in linear model.

### CONCLUSION

Before beginning an ecological parameters investigation, each scientist must select, what kind of biological parameters to measure in order to measure all the essential parameters simultaneously. Following the results, since 1998, we consider whether maturity may appear as the main factor in linear model for lindane. Still there are relatively strong arguments regarding uniqueness of the individual catches. There are incomparable sets of factors determining lindane in each area and year.

### REFERENCES


### TABLE 1. Summary of the different HCH concentrations and calculated depositions at the stations [7]

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Station</th>
<th>Air (pg/m³)</th>
<th>Precipitation (g/l)</th>
<th>Deposition (g/m² d)</th>
</tr>
</thead>
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<tr>
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<td>Drzowno-Poland</td>
<td>72 (n=5)</td>
<td>0.63 (n=2)</td>
<td>1.4 (n=2)</td>
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<tr>
<td>54°15'</td>
<td>Swibno-Poland</td>
<td>103 (n=6)</td>
<td>8.65 (n=3)</td>
<td>5.7 (n=3)</td>
</tr>
<tr>
<td>55°25'</td>
<td>Ventes R.-Lithuania</td>
<td>26 (n=10)</td>
<td>1.63 (n=15)</td>
<td>7.3 (n=15)</td>
</tr>
<tr>
<td>56°14'</td>
<td>Oland-Sweden</td>
<td>20 (n=21)</td>
<td>2.5 (n=13)</td>
<td>0.98 (n=13)</td>
</tr>
<tr>
<td>56°17'</td>
<td>Broneh-Sweden</td>
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<td>1.8 (n=12)</td>
<td>1.9 (n=12)</td>
</tr>
<tr>
<td>56°50'</td>
<td>Salaspils-Latvia</td>
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<td>1.3 (n=15)</td>
<td>2.5 (n=15)</td>
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<tr>
<td>58°20'</td>
<td>Vilsandi-Estonia</td>
<td>33 (n=28)</td>
<td>2.1 (n=5)</td>
<td>3.7 (n=5)</td>
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<tr>
<td>59°21'</td>
<td>Gotska s.-Sweden</td>
<td>45 (n=24)</td>
<td>1.4 (n=15)</td>
<td>2.2 (n=15)</td>
</tr>
<tr>
<td>59°17'</td>
<td>Stockholm s.-Sweden</td>
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<td>1.3 (n=10)</td>
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<td>0.22 (n=10)</td>
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<td>Kalix-Sweden</td>
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<td>0.33 (n=14)</td>
<td>0.16 (n=14)</td>
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<tr>
<td>All stations</td>
<td>25 (n=275)</td>
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<td>1.3 (n=178)</td>
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</table>
THEME III: WASTE TECHNOLOGIES

POLISH EXPERIENCE ON SITE REMEDIATION FOLLOWING REMOVAL OF UNDERGROUND PESTICIDE STOCKS – LEGAL AND FEASIBILITY ASPECTS

STANISŁAW STOBIECKI, KAZIMIERZ WALECZEK, TOMASZ STOBIECKI, ANDRZEJ SIŁOWIECKI, IRENA GIZA

Plant Protection Institute, Sośnicowice Branch

SUMMARY

For the past nine years Poland has dealt with the issue of disposal of obsolete pesticides and other pesticide waste stored underground and in old warehouses. Close to 9,000 tons of obsolete pesticides have already been disposed of. It is estimated that we still have 7,000–9,000 more and according to the implementation plan outlined by the Stockholm Convention they should have been removed by the year 2010 and, by then, the problem should have been resolved. The disposal companies have gathered a lot of experience in the field. One of them is the Plant Protection Institute, which has neutralized a total of around 1,000 tons of waste.

The process of underground storage removal consists of four stages:

- Excavation of waste.
- Thermal neutralization.
- Demolition and neutralization of underground storage structure.
- Site reclamation.

Site remediation aims at restoring the quality of contaminated soil to the condition that complies with the quality standards specified by legal regulations. It also restores the natural form and shape of the site. If the underground structure is not tight and contaminants leak into the surrounding soil and water and then migrate further away, the problem becomes very complex. Estimating the real threat to people and the environment then depends on the hydrogeological profile. The standards specify the permissible levels of contaminants, although technical and economic aspects can make compliance unrealistic.

After the primary contamination source has been removed, i.e. after the site is clean of pesticide waste, the health and environmental risk assessments should be conducted for humans and animals, revision of the site status against legal regulations regarding the land preservation and classification of soils should come next, followed by the selection of the appropriate method of remediation. An individual approach towards each site is important because of site-specific features like its geological structure and different compositions of the pesticide waste.

I. INTRODUCTION

The use of pesticides in agriculture, besides its major purposes (to prevent losses caused by weeds, pests and diseases and improve the crop quality), creates a lot of environmental problems. One of them is pesticide waste. The major threat is posed by obsolete waste pesticides, stored in different places, in underground storage tanks (hereafter called “tombs”) or directly dug into the ground. Such places do not comply with any requirements regarding hazardous waste storage facilities.

In Poland, in the beginning of the 1970s large quantities of pesticides were collected that for various reasons could no longer be used for preventive treatments. Poor pesticide economy and too much state subsidy to pesticide users are to blame for the problem. The pesticides were cheap and this lead to overstocking. The Polish problem of obsolete pesticides has been brought up to international attention several times. It is well documented and published in many scientific and popular magazines. The problem was revealed in the early 1990s. Back then, the total amount of obsolete pesticides was estimated to be around 60,000 tons in 343 tombs. These early estimates were then revised during a partial national inventory.

Since 1996, tomb removal projects have continued and as a result a total of 110 tombs containing around 9,000 tons of waste were disposed of. It is estimated that there are 166 more tombs in Poland waiting to be remediated with around 7,500 tons of waste. The priority list includes 51 facilities. The pesticides contained substances that are currently banned from use. The tombs store chemicals composed of 9 out of 12 substances that belong to the so called “persistent organic pollutants” (POPs), disposal of which is mandated by the Stockholm Convention.

At the end of 2004, Poland completed the Convention implementation program and included the tomb disposal as one of its major objectives. The obsolete pesticides are planned to be removed by the end of 2010. Currently, it is important that the work ahead of us is well organized and carried out according to the hazard hierarchy: comprehensively, i.e. the clean-up must also include the existing effects of contamination; and with proper utilization of public funds available for the project, both domestic and foreign.

Currently, the tomb disposal projects rely on the market economy. Due to the fact that tombs are not a private liability, the local authorities are in charge of public tendering, with the Inspectorate for Environmental Protection supervising the disposal process. National funds are used for the projects, with major contributions from the National Fund
for Environmental Protection and Water Economy and its provincial offices. There are cases of local initiatives, where township officials allocate and use the money for the projects.

The disposal method currently used for the waste is thermal neutralization, taking place nationally. Contaminated soil and concrete structures are neutralized at hazardous storage facilities. This phase of disposal is key to the success of the entire undertaking because it is intended to protect the environment - especially surface and underground water - against the secondary contamination caused by polluted soil. This secondary contamination is present at every tomb disposed of so far, due to their leaking construction. The legal regulations regarding site remediation give a possibility for different interpretations, which can be very damaging as regards the ecological effects and the rational use of public resources.

II. TOMBS AS A POINT SOURCE OF SOIL CONTAMINATION

Tombs constructed in the 1970s were intended as pesticide waste’s final destination. They stored pesticides withdrawn from the market, pesticides that could no longer be sold and empty containers. Implementation of the Instruction No. 1/71 created a network of tombs throughout the country. Tombs had three major types of design:

1. Wells made of concrete rings 1m in diameter and up to 3 m deep,
2. Wells made of concrete rings with diameter of 2.1 m and up to 3 m deep and
3. Concrete underground cubicles.

Photos 1 to 3 show typical tombs. In practice, besides the typical tombs, military bunkers were adapted for waste storage, and sometimes the pesticides were dug directly in ground pits. The inside and outside walls of the wells were supposed to be insulated with tar, and the leak-proof bottom was to be sealed with a 10 cm concrete layer. The site was to be marked and fenced and the containers set and sorted in order. Illustration 1 shows the tomb structure.

In several cases, the reality proved to be totally different: tombs were constructed of poor-quality materials, wells were not insulated, the locations were randomly picked and not documented, waste in bulk was thrown into wells and mixed with some containers intentionally destroyed to prevent identification, wells were poorly constructed. After decades it turned out that this “disposal method” did not provide a permanent solution to the problem, but as the compounds leaked into the adjacent surroundings they contaminated soil and underground water.

The materials stored in tombs are usually a mix of pesticides and containers, sometimes a mix of medical and chemical substances. They make up a semi-fluid mass, which is impossible to sort out, and consist of both the pesticide’s active ingredients and the products created as a result of their reactions. All this is mixed with broken glass, metal, plastic, aluminium and wooden parts and pieces, making up waste of a very complex composition.

After 30 years, concrete can no longer be a sufficient barrier for leaking contaminants, which makes the tombs an active source of chemical pollution for soil and water. The contaminants permeate further spreading into underground water and drinking water intakes. Underground waters are at the highest risk and they get contaminated first.

The locations of tombs show much variation in terms of hydrogeology and environmental impacts. The systems of protection, both from top and bottom, are different, too. The degree of protection from top regulates the amount of precipitation going into the tomb and creating the medium for carrying the contaminants out. The bottom sea – both the well insulation and geological structure is key for the actual flush-out and spread of the contaminants into the environment. The amount and rate of contaminants release is also connected to the amount of stored pesticides, their quality (damaged or sealed containers) and the type of waste and preparation (solids or dusty, easily soluble in water).

The flow of underground water spreads the chemicals and causes much environmental damage, which is well researched and documented in several locations. The direction and range of contamination is very difficult to assess. With favourable hydrogeological conditions and insulating ground layers, the contaminants may be halted close to the primary source of pollution and cause only a local hazard. An example of a relatively well-located tomb was found in Julków, township of Skierniewice.

The 450 m² tomb was located at the southern end of a landfill in Julkow, at a former gravel pit. There were 30 wells located on the fenced and marked site, 1.50 – 1.60 m deep and inside perimeters of 0.9 to 1.00 m. Based on the geological profiles it was assumed that the main water level
was reached by drilling at the depth of 26 – 28 m and it was covered with several meters of boulder clay layer. This location of the tomb made it hard for the leaking chemicals to spread, so the contamination was limited to a very small area. After removal of waste, tomb concrete structures and most contaminated soil, the remediation phase began. Samples taken at the location allowed to determine the extent of contamination and decide on further work.

Table 1 and Illustration 2 show the examples of pesticide determinations from soil samples taken at the tomb in Julkow and sampling diagram.

An example of a really badly located tomb is that of Niedzwiady, which was built in 1974 according to a typical design, i.e. using concrete rings and chambers. In 1992 it was decided to assess its technical condition. Holes were drilled around the tomb and with the direction of the underground water flow. The soil samples revealed presence of active substances, which indicated a leaking structure. The tomb was built on fine sands and dusts with underground water levels at 5 – 6 m below the surface, and the direction of water flow was towards the drinking water intakes. A decision was taken to remove the tomb. In 1996 the removal began. Two cubical chambers with total capacity of 90 m³ and 8 wells were found around the site. They contained 65 tons of waste. Soil layers were sampled as the structures were being removed and the highest concentrations of biologically active ingredients reaching a few percent were found just below the bottom of the chambers. The water collected in the trench had several hundred mg/dm³ of bioactive ingredients.

Observations of samples from the piezometer network indicated that the range of toxic concentrations around the site exceeds 200m, and the range of tomb contamination reaches 350 – 400 m. Illustration 3 shows the diagram of contaminants removal and sampling around the Niedzwiady tomb.

Table 1: Soil analyses – Julkow (during remediation)

| Bio-active ingredient | Determination limit for soil mg/kg | G-1 11/03 | G-1 12/03 | G-2 13/03 | G-3 14/03 | G-4 15/03 | G-5 16/03 | G-6 17/03 | G-7 18/03 | G-8 19/03 | G-9 20/03 | G-10 21/03 | G-11 22/03 | G-12 23/03 | G-13 24/03 | G-14 25/03 | G-15 26/03 |
|-----------------------|-----------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| ΣDDT*                | 0.005 + 0.005 mg/kg              | 0.322     | 0.345     | 0.370     | 0.395     | 0.420     | 0.445     | 0.470     | 0.495     | 0.520     | 0.545     | 0.570     | 0.595     | 0.620     | 0.645     | 0.670     | 0.695     |
| Aldrine              | 0.005                            | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     |
| Dieldrin             | 0.005                            | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     |
| α-HCH                | 0.005                            | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     |
| β-HCH                | 0.005                            | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     |
| γ-HCH                | 0.005                            | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     |
| Heptachloroethane    | 0.005                            | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     |
| Chlorofenol          | 0.005                            | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     |
| Atometra             | 0.005                            | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     |
| Simazine             | 0.005                            | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     |
| Maceh-diet C₂⁰       | 0.005                            | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     | 0.005     |

Illustration 2: Soil sampling diagram – Julkow

Table 2: Results of pesticide determinations from underground water samples (Niedzwiady)

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Determination limit mg/L</th>
<th>Well at the site (S) mg/L</th>
<th>Piezometer N1 mg/L</th>
<th>Piezometer N2 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lindane</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Dichloroethane</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>2,4-D</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>MeHAT</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Illustration 3: Site plan – Niedzwiady
Results of analyses of water samples taken from piezometers around the tomb in Niedzwiady – Table 2.

The examples just described are characteristic of two most commonly encountered cases: the first one of a relatively less hazardous tomb with contamination concentrated close to the tomb, the other one – highly toxic and contamination, spreading through ground structures.

It should be noted that even after the tomb contents, its chambers and adjacent ground are removed, the soil around the site could be still contaminated. If the hazard is significant, the site should be remediated.

III. SITE REMEDIATION AFTER THE DISPOSAL OF CONTAMINATION SOURCE – LEGAL ASPECTS

According to Polish regulations, remediation as a result of improper reshaping of a site natural setting means the site reconstruction to its previous state, whereas remediation of a site with contaminated soil means restoring the soil until it meets the required quality standards. In the case of remediation after the removal of a tomb, which usually creates a strong point contamination limited to a small area, efforts focus on preventing the surface and underground water pollution with contaminants permeating through the soil, and then restoring the soil quality to meet the standards.

The issue of soil remediation in the European Union is considered a strategic task within the field of environmental protection. The currently drafted European Strategy for Soil Protection is based on the document by the European Commission of April 16, 2002 “Towards a Thematic Strategy for Soil Protection”, accepted by the European Parliament on October 10, 2003. The document outlines the strategy framework, which cannot be universal for the entire EU, because of different conditions in different member countries. Special emphasis is put on the elimination of dispersed contamination regarded as the major source of progressing soil degradation throughout the regions of Europe. The Document does not offer sufficient tools to handle the kind of problems arising from the very complex condition of point contamination as in the case of tomb removal, and it leaves the details of legal regulations up to the individual member countries.

The Netherlands, Germany and Great Britain were the first countries to introduce quality standards as legal acts. The Dutch approach, as included in the regulations of 1995, was to unify the quality standards for all types of soils, with no regard to the type of use. This approach turned out to be extremely costly when it came to its practical application. The new approach, which takes into account the use of a site and classifies the soils accordingly, is reflected in German laws of 1998 and British regulations.

Polish legislature follows this approach. The first regulations concerning permissible contamination levels (without naming the specific pesticides) and describing their handling during disposal were published in 1994 by the State Inspectorate for Environmental Protection (POL: PIOŒ) as a set of recommendations titled: “Methodological guidelines for estimating contamination levels of soil and underground water contaminated with oil derivatives and other chemicals during remediation process”. The recommendations were not legally binding, which paradoxically was beneficial for untypical point contamination sources, like the tombs.

Right now, the basic legal act regarding the quality standards is the “Executive Order concerning the quality standards for soil and ground” of September 9th, 2002 issued by the Ministry of Environmental Protection. The Executive Order differentiates between various permissible contamination levels of different substances depending on the type of site use, depth of soil sampling and site properties (water permeability). From the point of view of remediating a site after tomb removal, it is important that the Order introduces the pesticide concentrations, which was not included in the original recommendations by PIOŒ.

The following Table 3 includes the values of pesticide contamination limits selected from the above-mentioned Order.

The competence and duties of local authorities and parties liable for site restoration during the remediation process are regulated by “The Environmental Protection Law” of April 27, 2001. The Act makes the owner or the polluter responsible for the cleanup, with appropriate environmental authorities setting forth the standards for the remediation process. The cleanup is carried out based on an administrative decision. The Law also indicates that the assessments of soil and water quality are performed as part of the state environmental monitoring, with periodic testing being the responsibility of township officials or property owners.

In practice, the implementation of the regulations proved them insufficient, and some complex projects, like tomb removal with accompanying site contamination, exceed the competence of

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**Table 3: Permissible contamination levels (mg/kg of dry mass)**

<table>
<thead>
<tr>
<th>No.</th>
<th>Contaminant</th>
<th>Group A</th>
<th>Group B</th>
<th>Group C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Depth [m]</td>
<td>Ground permeability [m/s]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0-0.3</td>
<td>0.3-1.5</td>
<td>&gt;1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>up to</td>
<td>below</td>
<td>up to</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10×10⁻²</td>
<td>10×10⁻²</td>
<td>10×10⁻²</td>
</tr>
</tbody>
</table>

### V. PESTICIDES

#### V/A Chlorinated organic pesticides

<table>
<thead>
<tr>
<th>No.</th>
<th>Contaminant</th>
<th>Group A</th>
<th>Group B</th>
<th>Group C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,1-DDE</td>
<td>0.0025</td>
<td>0.0025</td>
<td>0.0025</td>
</tr>
<tr>
<td>2</td>
<td>Aldrine</td>
<td>0.0025</td>
<td>0.0025</td>
<td>0.0025</td>
</tr>
<tr>
<td>3</td>
<td>Dieldrin</td>
<td>0.00005</td>
<td>0.00005</td>
<td>0.00005</td>
</tr>
<tr>
<td>4</td>
<td>Eindrin</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>5</td>
<td>α-HCH</td>
<td>0.0025</td>
<td>0.0025</td>
<td>0.0025</td>
</tr>
<tr>
<td>6</td>
<td>β-HCH</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
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<tr>
<td>7</td>
<td>γ-HCH</td>
<td>0.000005</td>
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#### V/B Pesticides non-chlorinated

<table>
<thead>
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<th>No.</th>
<th>Contaminant</th>
<th>Group A</th>
<th>Group B</th>
<th>Group C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Carbaryl</td>
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<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>2</td>
<td>Carbofuran</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>3</td>
<td>Maneb</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>4</td>
<td>Thiram</td>
<td>0.000005</td>
<td>0.00005</td>
<td>0.00005</td>
</tr>
</tbody>
</table>

Site types:
- **Group A** – protected sites, as included in the water law and environmental preservation laws (e.g. national parks).
- **Group B** – agricultural use, forestry, residential and commercial construction areas, excluding industrial uses.
- **Group C** – industrial, mines, main transportation routes.
officials issuing the decisions regarding the scope and way of remediation. In response to the concern, in the end of 2004 the Main Inspectorate for Environmental Protection issued a set of guidelines for administrators “Assessing sites with unmet soil quality standards” with recommendations for law interpretation, remediation methods, and contamination level testing, including sampling places and methods as well as recording the results. Temporarily, the guidelines are intended to close the loophole in the regulations till the now much needed Act is being revised and appropriate amendments are issued regarding contamination limits and site contamination testing procedures.

IV. PRACTICAL PROBLEMS ACCOMPANYING THE PROJECT IMPLEMENTATION IN POLAND

The basic method used for remediating the soil contaminated with pesticides is replacement. The contaminated soil is excavated and transported to a hazardous waste facility, where it undergoes a long-term natural biological and physico-chemical process of self-cleansing in safe conditions. This method is expensive due to high cost of storing and transporting the materials, treated as hazardous waste (around 100 euro/Mg). In the case of contaminants spreading deep and wide throughout permeable ground this method is highly impractical. In such cases, when the contaminants reached the water-bearing surfaces, theoretically a different method can be applied: that of creating a natural site depression, then pumping out the contaminated water and cleaning it afterwards. This solution, used for post-military sites contaminated with oil derivatives has not been practically applied for pesticide-polluted areas.

Other biological and physicochemical methods, “in situ” and “ex situ”, are also insufficient and have not been tested out in practice. The need for new methods is growing and there are many companies searching for them or adapting foreign inventions. With that in mind, the Ministry of Environmental Protection is working on a collection of cleanup and remediation methods that will be published as a database with information on different companies, remediation types and service prices. The project is performed jointly by the Institute of Environmental Protection in Warsaw and the Institute of Ecology and Industrialized Areas in Katowice and should be completed by the end of 2005.

It should be emphasized that each of the pesticide disposal methods is expensive, which is an important problem for Poland. There is a chance of tapping into the EU funds available for these types of projects. However, parties applying for them must acquire expertise in assessing the scope of contamination, selecting the appropriated disposal method, etc, as well as legal aspects.

Based on our experience, it is important to note that each case of underground water contamination with pesticide active ingredients needs to be carefully assessed, especially with respect to possible contamination of underground sources of drinking water, taking into account the site-specific physical and chemical ground composition and geological profile. After the contamination source is removed, the site needs to be monitored for its migrating contaminants. When the risk is assessed, a decision regarding the appropriate remediation method can be taken. The method based on risk assessment studies should be the law. Methods of handling a problem based on prior risk assessment are commonly applied in health and environmental risk studies, even though there are no unified rules of application of the methods.

Following blindly the current regulations mandating the restoration of soil standards to meet the requirements can lead to unnecessary use of scarce funds for sites with little or no environmental hazard, at the cost of sites that require immediate cleanup and remediation. In some cases, badly written laws can result in intentional cover-ups of contaminated sites and taking no action for the fear of spending additional money. In Poland, a reasonable management of limited resources is of great importance.

The next steps, involving remediation of sites contaminated with pesticides, should focus on the following basic activities:
- modification of current legal regulations
- careful monitoring of pesticide contaminants
- establishing a system of methods and technologies available for soil cleansing

These activities have already been initiated.

V. CONCLUSIONS AND PRACTICAL RECOMMENDATIONS

1) Solving the problem of ground point contamination due to a leaking tombs containing obsolete pesticides requires a special and individual approach.

2) Special attention should be given to proper identification of the range, type and level of contamination. The observation points (piezometers) should be located after a detailed hydrogeological study around the site. Additional drilling is also necessary.

3) Despite standard pesticides, like sum of DDT isomers, a-, b-, g-HCH, fenitrothion, methyloparathion, toxaphene, 2,4-D, atrazine, chemical analyses should include other active ingredients and, in some cases, their reaction products.

4) Highly sensitive methods need to be used for testing. For water the detestability limit is set for drinking water standards (below mg/litre).

5) The results of the study should help analyze the situation from the legal perspective regarding soil protection.

6) Further remediation activities should not commence without performing health and environmental risk assessments for humans and animals.

7) The risk analysis should consist of the key elements and must take into account the specific nature of pesticide contamination.

8) The selection of an appropriate remediation method, based on a risk analysis, should consider the technical capabilities and economic conditions. The criteria of a successful ecological outcome must be precisely described.

9) There is a lack of international guidelines for the disposal of point contamination of soil with pesticides.

10) It is crucial to establish a monitoring network to observe the site condition after its cleanup and remediation.
THE USE OF ALTERNATIVE TECHNOLOGIES FOR THE TREATMENT OF HAZARDOUS WASTES

Christophe Rittersberger
Tredi International, France

INTRODUCTION
Tredi has developed with its Research Department, over the past 15 years, new solutions for the treatment of highly hazardous wastes: Thermal Process
• Thermal vacuum extraction
• Thermal desorption
• Catalytic hydrogenation and wet air oxidation
• Autoclaving
• Incineration

Chemical Process
Physical Treatment
• Filtration
• Solvent extraction

Biological degradation.

THERMAL VACUUM EXTRACTION
The system is designed to reach in vacuum conditions feed material temperatures of up to 400°C allowing an effective treatment of soils and sludge polluted with a wide range of low and high boiling point compounds. The system is suitable for PCBs and mercury.

The gases produced during the process are treated by a vapour recovery system which includes a condensing unit and a vapour phase carbon adsorption unit. The condensed mixture is incinerated
The process applications include the treatment of PCBs contaminated soils and of a full range of chlorinated hydrocarbons, organochlorine pesticides.

This technology is not applicable for treatment of liquids (water, flammable liquids and solvents), and materials that cannot be decomposed by thermal treatment at 600 °C.

The TREDECO Unit used for the treatment and destruction of contaminated soils in 2001 in Denmark.


**CATALYTIC HYDROGENATION AND WET AIR OXIDATION**


**AUTOCLAVING**

PCB oils and solids decontamination by liquid – liquid extraction using a third part solvent
Apparatus in service on the site of St Vulbas

Optimisation by recycling of the third part solvent (perchlorethylene)

INCINERATION

**INCIERATION**

**Rotary Kiln**

<table>
<thead>
<tr>
<th>PCB and halogenated wastes</th>
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**Static Kiln**

<table>
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<th>specific kiln for liquids PCB</th>
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GAS CLEANING

Gas cleaning facility for both kilns

<table>
<thead>
<tr>
<th>HCl</th>
<th>10 mg/Nm3</th>
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<tbody>
<tr>
<td>HF</td>
<td>&lt; 1 mg/Nm3</td>
</tr>
<tr>
<td>SO2</td>
<td></td>
</tr>
</tbody>
</table>

CHEMICAL TREATMENT

Substitution Reaction

- for the treatment of low level PCBs wastes usually between 50–2000 ppm
- the process involves the treatment of the PCB with NaH (Sodium Hydrid)
- a mobile installation using this process is working in Europe since about 10 years.
Treatment rates: up to 1000 l/h, depending of PCBs initial concentration

Works directly at the feet of the transformer

Transportation doesn't need extra weight
Standard trucks are used

PHYSICAL TREATMENT

This microfiltration process is operational since two years at TREDI Saint-Vulbas Plant.


SOLVENT EXTRACTION
Solvent Extraction techniques are cost-effective methods to treat PCBs and other chlorinated compounds, but the main limitation is that the contaminants transferred to another phase must be destroyed through a secondary method. TREDI has tested a carbon dioxide extraction in supercritical conditions.

CO₂ extraction technology has been tested to soils and to transformers contaminated with PCBs.

Zaragoza, R., Blanchard, J.M. & Barna, L. (1997). Supercritical fluid extraction applied to soils contaminated by chlorinated compounds. 4th Meeting on Supercritical fluids and Environment. 20-21 January 1997, INSA Villeurbanne, France

BIOLOGICAL DEGRADATION
Enhanced bioremediation, also called biostimulation or bioaugmentation, is a process to increase the biodegradation rate of contaminated soil by the addition of nutrients and oxygen.

Lab scale trials proved very successful
At TREDI Saint-Vulbas, Pilot plant trials had proven successful at a PCB concentration limit of 60% of chlorine. Over 60% PCB's are not easily biodegradable.

Lab scale and pilot plant at TREDI Saint-Vulbas
CONCLUSIONS
The difference between technologies that only separate and/or concentrate a pollutant (e.g. solvent extractions, thermal desorption, filtration) and those which destroy the contaminant (e.g. oxidation, reduction, and biodegradation) must be considered when setting site remediation goals.

The applicability and availability of the different treatment technologies depend on the location of treatment systems and whether the waste can be transported to the treatment facility.

Social, environmental, technical and economical criteria should be considered during the technology process selection.

THERMAL DESTRUCTION OF OBSOLETE PESTICIDES

Kåre Helge Karstensen

The Foundation for Scientific and Industrial Research (SINTEF)

1. INTRODUCTION
Combustion and other forms of thermal treatment have, over the years, been adopted as proven technologies to dispose of hazardous waste, municipal solid waste, and medical waste regulated under the Resource Conservation and Recovery Act RCRA and toxic substances under the Toxic Substances Control Act TSCA (Lee et al, 2000; Dempsey and Oppelt, 1993). Pesticides and obsolete pesticides constitute a considerable part of the compounds regulated under the TSCA (Ferguson and Wilkinson, 1984). Pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest. Pests are living organisms that occur where they are not wanted or that cause damage to crops or humans or animals. Though often misunderstood to refer only to insecticides, the term pesticide also applies to herbicides, fungicides, and various other substances used to control pests (Pesticide Manual 1997).

Combustion temperature and residence time needed for mixed hazardous wastes cannot be readily calculated and are often determined empirically. Some common solvents such as alcohols and toluene can easily be combusted at lower temperatures, while other more complex organic halogens require more stringent conditions such as the United States Environmental Protection Agency (US EPA) Toxic Substances Control Act (TSCA) PCB incineration criteria of 2 seconds residence time at 1200 °C and 3 % excess oxygen in the stack gas (Federal Register, 1999) or the European Council Directive 2000/76/EC on the Incineration of Waste criteria of 1100 °C for at least two seconds if more than 1 % of halogenated organic substances are incinerated (Council Directive, 2000).

Combustion is a combination of pyrolysis and oxidation. Pyrolysis is a chemical change resulting from heat alone and involves the breaking of stable chemical bonds, often resulting in molecular rearrangement. Oxidation is the gross reaction of an organic species with oxygen and requires relatively low activation energies (Niessen, 1995). For efficient combustion, oxidation should be the dominant process, with pyrolysis occurring either incidentally to the oxidation or to put a material into a better physical form for oxidation. To combust hazardous wastes effectively, pyrolysis must be efficient and complete before oxidation of the molecular chemical by-products can occur.

To achieve a complete thermal destruction, sufficient temperature, oxygen supply, residence time and mixing conditions are needed (Brunner 1993; Dempsey and Oppelt, 1993). Thermal treatment of hazardous wastes and chemicals has traditionally been done by using dedicated hazardous waste incinerators and/or cement kilns. Both of these technologies can achieve a complete thermal destruction of mixed hazardous wastes, but normally cement kilns have higher temperature and longer residence times than incinerators (Freeman, 1997). A cement kiln will provide flame and kiln gas temperatures up to 2000 °C and long residence times up to 8 seconds will ensure complete pyrolysis and surplus oxygen ensures complete oxidation (Freeman, 1997).

2. THERMAL DESTRUCTION OF PESTICIDE WASTES, POPS AND OTHER HAZARDOUS CHEMICALS
The pesticide manufacturing industry started early to look into possible management and treatment options for obsolete pesticides and pesticide wastes and in the 1970’s and 1980’s a number of research and demonstration studies were conducted to identify the best disposal options for pesticides and pesticide wastes. Combustion was soon considered to be the best method and several key research projects confirmed this in pilot and commercial available incinerators (Ferguson and Wilkinson, 1984).

In a study comparing chemical and thermal methods for disposal of 20 pesticide chemicals Kennedy et al (1969) concluded that incineration is superior to chemical methods for the destruction of pesticides and that most pesticide compounds are destroyed effectively by burning at temperatures 800 °C to 1000 °C (Atkins, 1972).

In 1977 the US Air Force incinerated 8.7 million liters of Agent Orange and the destruction efficiency was estimated to be at least 99.99 % (Ackerman et al, 1978).

General Electric incinerated 6000 liters of 20 % liquid DDT formulations with temperatures ranging from 870 °C to 980 °C and retention time of up to 4 seconds achieving destruction efficiency better than 99.99 % (Leighton and Feldman, 1975).

DDT and 2,4,5-T formulations constituting 20 % of the solid input were destroyed in a municipal sewage sludge
incinerator with an average temperature ranging from 600 °C to 690 °C and destruction efficiencies from 99.95 % to 99.99 % (Whitmore, 1975).

The University of Dayton achieved destruction efficiencies exceeding 99.99 % at 2 seconds retention time for DDT, DDE, Dieldrin, Endrin, Hexachlorobenzene, Kepone, Mirex and Pentachloronitrobenzene in an incinerator operating at 900 °C (Duvall and Rubey, 1976).

The Midwest Research Institute carried out pilot studies on thermal decomposition of Aldrin, Atrazine, Captan, DDT, Malathion, Mirex, Picloram, Toxaphene and Zineb in 15 liquid and solid formulations and the destruction efficiencies generally exceeded 99.99 % over a range of temperatures and retention times; 950 °C to 1100 °C, 1.2 and 6 seconds (Ferguson et al, 1975).

In a study for the US Army, TRW Systems investigated the thermal destruction efficiencies of Chlordane, 2,4-D, DDT, Dieldrin, Lindane and 2,4,5-T at a temperature of 1000 °C and 0.4 second retention time. The destruction efficiencies exceeded 99.99 % (Shih et al, 1975).

The Los Alamos National Laboratory investigated for US EPA the thermal destruction efficiencies of Pentachlorophenol at a temperature of 980 °C and 2.5 second retention time. The destruction efficiencies exceeded 99.99 % (Stretz and Vavruska, 1983).

In a review of incineration options for pesticide wastes, Oberacker (1988) lists ranges of pesticide formulations of DDT, Aldrin, Dieldrin, Malathion, Toxaphene, Atrazine, Captan, Zineb, Mirex, Herbicide orange (including dioxins and furans), PCP, Kepone and Chlordane and their thermal destruction efficiencies in different incineration tests. The exceptions to the rule of achieving destruction efficiencies better than 99.99 % was when the pesticide concentration was very low (created problems with the analytical detection limits), when solvents were not properly mixed, when products of incomplete combustion (PIC’s) appeared or in cases where the temperature were deliberately reduced to determine the operational bounds of effective performance. Potential problems with certain heavy metals and compounds like bromine and iodine were questioned in the review. Some metals were included in the incinerator tests, including lead, zinc, arsenic, chromium and others, without creating any problems.

In 1989 Oberacker investigated the incinerability of Ethylene di-bromide (EDB), Dinoseb and 2,4,5-T. The EDB molecule contains approximately 85 % bromine by weight and earlier studies had resulted in visible bromine gas emissions from the incinerator stack when EDB was incinerated. This problem was solved completely in the US EPA test burn by adding 10 % dilute sulphuric acid. Approximately 75,000 liters of an EDB/ethylene dichloride and carbon tetrachloride mixture and 20,000 liters of an EDB/chloropicrin formulation were incinerated and all compounds achieved destruction efficiencies better than 99.9999 %. No bromine was detected in the stack, detection limit of 4.5 mg/m³. Two Dinoseb formulations were incinerated at a feeding rate of up to 180 liters per hour, achieving destruction efficiencies better than 99.999 %. The test results for 2,4,5-T was not ready when the article was written but EPA was confident that incineration was feasible.

In a study by Oberacker et al (1992) the air emissions and residues from open burning of used pesticide bags contaminated with Thimet and Atrazine in farm field conditions were characterised. While the amounts of particulates were high, the toxic releases appeared small in terms of posing any significant health or environmental risk.

The US EPA also carried out a number of studies on industrial organic hazardous wastes in different incinerators and the following compounds were found to be incinerable to the 99.99 % or better destruction level: PCB’s, Toluene, Tetrachloroethylene, Trichloro-ethylene, Carbon tetrachloride, Naphtalene, Chloroform, Methylene chloride, Methyl ethyl chloride, Phenol, Benzene, Butyl benzyl phthalate, Chlorobenzene, 1,1,1-Trichloro-ethane, Aniline, Benzyl chloride, Diethyl-phthalate, Phthalic anhydride, Amines, Chlordane, Chlorobzenes, Chloromethane, Chloroethanes, Cresols, Dimethyl phenol, Dodecanol, Hexachlorobutadiene, Isocyanates, Methylenyl bromide, Methyl pyridine and Phosgene gas (Oberacker, 1988).

The incinerability of pesticides and hazardous wastes were also investigated in different high temperature production processes, like brick kilns, cement kilns, oil furnace process, blast furnace, lime kilns, glass kilns etc. The conclusion of the study showed a limited potential for the use of most of these facilities for pesticide treatment, with the exception of cement kilns (Hall et al, 1983).

The details of cement production and experiences with co-processing hazardous wastes in cement kilns are described in part 1 of this article series.

3. DISCUSSION

Less than 1 % of the estimated accumulated amounts of obsolete pesticides spread around the globe have been disposed of since the beginning of the 1990’s. The bad management of hazardous chemicals constitutes a serious threat for health and environment and needs to be dealt with in a cost-efficient and responsible way.

Cement kilns are being used for environmentally sound management of hazardous wastes and chemicals in many countries and testing of cement kiln emissions for the presence of organic chemicals during the burning of hazardous materials has been undertaken since the 1970s, when the practice of combusting wastes in cement kilns was first considered. However, not all kilns are suited without upgrad ing or modifications and the feasibility should be assessed in case by case.

Already in the 1970’s the pesticide industry knew by practice that even persistent compounds were completely destroyed at combustion temperatures below 1000 °C and a few seconds retention time. Laboratory studies as well as thermodynamic and kinetic principles indicate that virtually all organic materials will be destroyed at temperatures exceeding 1000 °C for a reaction time of 2 seconds (Dellinger and Hall, 1986).

A cement kiln possess many inherent features which makes it ideal for hazardous chemicals treatment; high temperatures up to 2000 °C, long residence time, surplus oxygen during and after combustion, good turbulence and mixing conditions, thermal inertia, counter currently dry scrubbing
of the exit gas by alkaline raw material (neutralises all acid gases like hydrogen chloride), fixation of the traces of heavy metal in the clinker structure, no production of by-products such as slag, ashes or liquid residues from exit gas cleaning and complete recovery of energy and raw material components in the waste (Chadbourn, 1997).

Cement kilns have traditionally been associated with the emissions of high concentrations of dioxin and furan (PCDD/F’s) but this seems now to belong to the past. In a study performed by the World Business Council for Sustainable Development around 2200 PCDD/F measurements from wet and dry kilns, performed under normal and worst case operating conditions, and with the co-processing of a wide range of hazardous wastes fed to both the main burner and to the precalciner shows that most cement kilns can meet an emission limit of 0.1 ng TEQ/Nm³. The report also showed that 44 measurements from developing country cement kilns were far below 0.1 ng TEQ/Nm³ (Karstensen, 2006; UNEP, 2001).

A through feasibility study of the local cement kiln and a successful test burn will together with adequate safety arrangements, input control and operational procedures secure the same level of environmental protection in developing countries as in the EU and the US; i.e. there should be no reasons for not investigating the possibilities of using a local cement kiln in the future.

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METHOD FOR ECOLOGICAL UTILIZATION OF PESTICIDE RESOURCES WITH EXPIRED APPLICATION TERM BY THERMAL DESTRUCTION IN COKING MODE OF THE COAL BLEND

Dimitar Dimitrov, Vasil Popov

BACKGROUND

The actuality of the problem with pesticide resources is well known. Almost all of them, to a higher or lower extent, are dangerous for the environment and injurious to the human beings. In a number of models, intended to estimate the danger from different types of contaminants, pesticides are at the top of the list. Indicative of this is the circumstance that ⅔ of the entire express bulleting of toxicology and environmental protection is about them.

The problems with pesticides and their storage affect a number of European countries. This problem requires higher concentration and is becoming more complicated for Bulgaria, with a view to the parameters characterizing it and the approach selected by the Ministry of Environment and Water for solving it. According to the environmental report for the condition of the environment in Bulgaria for the year 2000, the quantity of stocks of obsolete pesticide is 4 931 tons. Poor storage conditions, lack of guards at the storehouses and lack of effective control all add to the potential dangers to human health. During 1999, the Ministry of Environment and Water (MEW) has undertaken measures for the solution of the problem in two directions:

1. By repacking and repairing the old storehouses and guarding the newly repaired storehouses, and by storing the old pesticides in “B-B” cubes.

2. Transportation of the pesticides to other countries.

Under execution of the project “Destruction of risk pesticides by Bulgaria and Holland” about 50 tons of pesticides are collected, transported and destructed in an incinerator in Rotterdam. The analysis of the two MEW concepts for solving the problem with old pesticides shows, that they have serious disadvantages.
Generally the problem is in postponing the problem and creating a new risk for the policy of environmental protection. The practice with "B-B" cubes has created a constant risk for the country and the negative effects will become more evident in the future. The second concept holds huge risks and difficulties, related to the packing in secured containers and different criteria for security of the different countries, as well as the difficult and long process of approval and coordination between the sending and receiving country. This is the concept of the findings in the article of Dr. Reiner Schuette “Pesticides kill” presented at the 7th International HCH and Pesticides Forum in Kiev in June 2003.

The method created by us is based on profound investigation of the scientific achievements in the field of coke-chemistry, agro-chemistry, toxicology, as well as on results from laboratory researches. The main idea during the creation of the method is the utilization of the pesticide resource under guaranteed safety of humans and environment by using an attendant process, such as coking of the coal blend.

**DESCRIPTION OF THE METHOD**

As it is known, coking of the coal blend is performed in a coke chamber with a volume of 22.5 m³ and dimensions: length 14.20 m, height 5.2 m, width 0.450 m. The entering coal blend in quantity of 20,000 kg is heated without air access from 50 to 1100 °C for 16-18 hrs, and then coke and gaseous substances are obtained as end products. The gaseous substances from the coke chamber enter a gas-container, where the gaseous products from all coke chambers of one coke battery are collected, under which a mixture with constant ingredients known as coke gas is obtained.

When heating the coals from 50 to 1100 °C in their organic mass, consisting of C, H, O, N and S, irreversible physic-chemistry changes set in, which are expressed by the term ‘thermal destruction’.

Thermal destruction is a versatile process, expressing the inter-relation between two types of competitive reactions: of destruction / decomposition in the initial structure of the source material / and of association (synthesis) of the inter-term products. These two types of reactions are mutually related and run during all phases of the system for a specified temperature. Their overcoming participation is represented by the tendency of the reacting substances to decrease isobaric – the isothermal potential of the system, as generating products, more thermo-resisting for a specified temperature, characterized by new structure of conjugation of the connections. From this point of view, after each increase in the temperature, more stable structures for the destruction in the different phases of the systems will appear, which will need a higher energy consumption, thus a higher temperature is needed and together with this longer duration of the heating.

The summarized data from the X-ray examination of the structure, infrared spectroscopy and nuclear-magnetic resonance determine that the molecule structure of the coals possesses high paramagnetic properties and high thermo-resistance, caused by the sections of poly-conjugation. An indicator for that are the kinetic curves, reflecting the mass loss during heating from 50 to 1100 °C. They show that at the end of coal coking, the coals lose from 18 to 23 % of their initial weight. From the analysis of the pesticide resources regarding their molecule structure and the type of chemical connections, as well as from the statistic data for their temperatures of decomposition, we determine that they are repeatedly thermally more unstable than the coals. Destruction of connections between the separate atomic groups in the molecule may be represented in descending order in the following direction: aromatic-naphthenes-heterocyclic-methylene-ester-anhydride-carboxile.

The chemical compounds, liberated in thermal destruction of coals, range over a very wide spectrum of the nomenclature of the organic compounds, particularly: acyclic and their derivatives – methane, olefines and nitro-compounds, derivatives of the carbon acid; carbamide, carbon sulphide; cyan compounds – dicyan, hydrogen cyanide; derivatives of benzole – benzole, toluene, xylene; polynucleus compounds with condensed aromatic nucleuses – naphthalene anthracene, cumarone, etc.; pyridine compounds; amines and their derivatives. It can be noted that over 800 compounds are identified in the coal tar only.

While investigating the technology for production of the environmental protection preparations, we have determined that almost all compounds contained in the coke gas are applied in the synthesis of the pesticide resources.

For example, on the base of cyclopentadien a great number of chlorine containing preparations are synthesized: chloride - Heptachlor, Aldrin, Dieldrin, etc. Carbon sulphide is extremely important for the production of large groups of fungicides, from derivatives of the dithiocarbamic acid – are obtained Ziram, pherbame, etc, from the creosol the preparations dinock, methylnitroflos, etc., from naphthalene – Dichlone, from pyridine – Diquat.

Considering that during decomposition of the pesticide resource, precipitation of CO₂, CO, CH₄ and unsaturated hydrocarbons is indisputable, then it is evident that the rest products will be analogous of the ones precipitated during coal coking.

In that way, utilization of 100 kg pesticide resource, added to 20,000 kg coal blend, will be performed in the coke chamber as a result of the process of thermal destruction.

Proceeding from the mechanism of the processes, during thermal destruction of the coals in the mode of coking, the pesticide subjected to the same conditions will decompose at temperature before the phase of semi-coke – about -500 °C, as the products of decomposition are analogous to those from the destruction of coals. Therefore, during UTILIZATION OF THE PESTICIDE RESOURCE AT THE TEMPERATURE MODE OF COKING FROM 50 to 1100°C THE GAS MIXTURE COMING INTO THE GAS-CONTAINER DOES NOT CONTAIN COMPOUNDS IDENTICAL WITH THE ACTIVE INGREDIENT OF THE PESTICIDE RESOURCE.

The applicability of the method for practical realization is motivated by the answers to the questions on the influ-
In order to answer these questions we have assumed the hypothetical treatment, that all the active ingredients of the pesticide resource under the coking mode remains unchanged and go into one of the end products of the material balance of the coking. We have directed the mathematic interpretation of data to one coke chamber and one coke battery (60 coke furnaces). The results from the analysis are effected in the patent and prove that under ratio 1:2000 of the active ingredient of pesticide resource to the coal blend, utilization does not influence the coke-chemical production in any qualitative or quantitative aspect.

The positive effect of utilization in the coke-chemical production is evident regarding caloricity of the reverse coke gas, which as result of precipitation of methane and olefins during utilization is increased. This is very important, as the reverse coke gas is used for blow-heating the coke furnaces and its increased caloricity improves the heating regime of coking.

The line diagram shows the technological cycle in a coke-chemical factory. Table 1 shows the ingredients of the coke gas, and Table 2 – the ingredients of the reverse coke gas. As it can be seen, the coke gas enters the gas-container at temperature of 750-800°C and cools to 90-100°C, and after cooling to 25-30°C in the ice-tubes it goes to the plants for capturing the chemical products. After capturing the chemical products the coke gas becomes poor or reverse one and by a special tube-line it is fed to the coke furnaces for blow-heating, where it burns. The whole cycle is closed and does not allow excretion of deleterious emissions. Based on the qualitative parameters of the material balance of coking and the treatment adopted, that the active ingredient of the pesticide resource remains unchanged and fully transfers into the coke gas we have determined, by mathematical statistical analysis, the interval from 1.3 to 3.2×10⁻⁴ in vol. % of the pesticide resource towards the total gas mixture. Even under such treatment, there is no danger to the environment and human health.

In order to define this conclusion as a necessary statement, we have referred to practical examples. Adding of different agents to coals during the last decades is directed to increasing the yield of chemical products from coking. We have experienced in practice conditions to apply additives to the coal blend of petroleum oil and coal-tar pitch in quantities of 100 to 300 kg and to put them under the coking mode. It is determined, that more aromatic compounds are obtained, which leads to increasing the yield of the raw benzene. The petroleum oil according to the classification of Acad. N. Melnikov is one of the first pesticide resources for plant pest control.

Generally, this refers to utilization of the pesticide resource by our mode in quantities several times greater than the ones we have set.

One of the most serious advantages of the method, which distinguishes it from the methods for burning, is the impossibility of forming dioxins during utilization.

We have given special attention to this question, because of the fact, that the dioxins are one of the most serious contaminants of the environment.

Some of their isomers are highly toxic, which makes them extremely dangerous to human health. Experts of the World Health Organization determine as daily doze from 1 to 4 pg for human’s weight per kilo. According to the classification of UNEP CHEMICALS emission sources of dioxins are in the following order: factories for production of iron and steel, initial and secondary production of copper, zinc and lead, thermo-electric power stations, burning installations, automobile transport, etc.

The capabilities of formation of dioxins in the temperature mode of coking of coal blend with added pesticide resource are:

1. At destruction of the active ingredient of the pesticide resource in the gas phase a compound with the chemical analysis of dioxins is to be liberated. This is impossible, because there is no pesticide in the practice, whose active ingredient is obtained on the base of the dioxin structure.

2. To synthesize toxic dioxin during the gas phase from the products of destruction of coals and the pesticide source.

We exclude the second possibility also, based on the conditions for synthesis of dioxins and the characteristic of the environment in the coking chamber.

The first dioxin was synthesized in 1957 under very special conditions – temperature, pressure, catalyst, and availability of a strong oxidizer and alkaline environment. In the coke chamber the process goes without access of air in a highly hydrogen environment. This property does not allow in the temperature mode of 50 to 1100°C, at any moment, a condition for synthesis of dioxins to be created. We have also investigated the hypothesis, however, that there is a compound with the chemical content of dioxin in the coke gas. With this hypothesis, that compound

<table>
<thead>
<tr>
<th>Ingredients of coke gas</th>
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<tbody>
<tr>
<td>Steam</td>
<td>250-450</td>
</tr>
<tr>
<td>Tar</td>
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<tr>
<td>BenzoI-hydrocarbons</td>
<td>30-40</td>
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<tr>
<td>Ammonia</td>
<td>3-13</td>
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<tr>
<td>Hydrogen Sulphide</td>
<td>6-25</td>
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<tr>
<td>Cyanogens-compounds</td>
<td>0.5-1.5</td>
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<td>Pyridine-compounds</td>
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<table>
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<tr>
<th>Ingredients of the reverse coke gas</th>
<th>volume %</th>
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<tbody>
<tr>
<td>H₂</td>
<td>55-59</td>
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<td>CH₄</td>
<td>23-28</td>
</tr>
<tr>
<td>CH₂</td>
<td>2-3</td>
</tr>
<tr>
<td>CO</td>
<td>5-7</td>
</tr>
<tr>
<td>CO₂</td>
<td>2-3</td>
</tr>
<tr>
<td>O₂</td>
<td>0.3-0.5</td>
</tr>
<tr>
<td>N₂</td>
<td>3-5</td>
</tr>
</tbody>
</table>
will be in the reverse coke gas, as the temperature of decomposing of dioxins is above 750°C. As it can be seen from the diagram, the reverse coke gas completes the cycle in the heating channels, where it burns under temperatures between 1300 and 1400°C, the circumstance predetermining the impossibility of appearance of dioxin in the environment.

Therefore, we have to note that there is no method from the famous ones, which can be defined as safe for the environment and people. The matter is in the risk degree and its decreasing to dimensions, determining its practical application. From this point of view, our solution to the pesticide problem has serious advantages against the other methods, as the factors determining the risk dimension are referring to elements out of the parameters of utilization.

At the practical level, the method is developed on an algorithmic base. In the technological regulations all steps with the corresponding sequence of implementation are outlined.

Specification of the software product and instructions for occupational health and safety are prepared. A financial plan is prepared, according to which utilization of 1 ton equals to 700 BGN. Also a schedule for utilization is prepared, consistent with the mode of charging the coke furnaces. Under the accepted mode for adding 100 kg of the plant protection preparations to the coal blend, it is possible utilization of about 3000 t from them to be performed in working mode of two coke batteries within two years. Our opinion is that a quantity of 100 kg is not optimal. It is possible to increase this number, but it is necessarily a process to be molded under laboratory conditions in two independent objects, as coking at different ratios of the pesticide resource and coal blend are made.

The result of the investigation of the content of coke gas would give the possibility to determine the optimal quantity of pesticide resource, subjected to utilization in the coke chamber. The above is of higher importance, as it shortens the time limit for solving the problem.

Regarding the practical realization of the work project under this method, we cannot omit one extremely important condition. This is the transfer of innovation technologies, i.e. the way from the creation to the implementation.

The complex regulative base, administration of a problem requiring an expert solution, unprofessional attitude of the responsible institutions, different assessment criteria, corruption – these are some of the holdbacks, which in many cases are insurmountable.

That is why the matter with destruction or utilization of pesticide resources in our country goes beyond the field of routine environmental problems and requires a higher level of social and political organization for its solution at national level.

This is also the position of famous experts, such as Prof. DSc. Galin Petrov – lecturer in organic chemistry, chemistry of pesticides and toxicology in the chemical faculty of Sofia University “Kliment Ohridski”, Prof. DSc. Mihail Haralampiev – senior inspector in the organization for prohibition and destruction of chemical weapons in Haga, Prof. DSc. Zahary Raikov – author of the theory for free radicals, by whose support this method is used.

The developed method is holding a patent for invention No 63753 from 03.12.2002, registered in the Patent Department of the Republic of Bulgaria and refers to “Utilization of pesticide resources with expired application term, in organic origin with unknown ingredients and in solid condition, by thermal destruction in coking mode of the coal blend”.

We have settled the limitation “in solid condition and in organic origin” in view of reaching maximum likelihood in the mathematical interpretation of statistic data from coking of coal blend with added pesticide resource to it. It is obvious from the conclusions we are representing, that the method is applicable for liquid and non-organic based pesticides. This is confirmed in practice with the technologies of coking with additives to the coal blend in quantities ten times higher than the ones set in our method. Furthermore, in 1996 an invention with European patent is registered, concerning the process for extraction of raw and liquid burning elements from used or waste plastics. Partial flow of this dipolymer in quantity of 400 kg is subject to coking with the coals.

In conclusion, universality of the method, safety of the utilization for people and environment, usage of an accompanying process, determining low rate of investments, as well as the expert level of support, are preconditions for surmounting the limits for its implementation.

124
RELEVANCE OF PCDD/PCDF FORMATION FOR THE EVALUATION OF POPs/PESTICIDE DESTRUCTION TECHNOLOGIES – CURRENT STATUS AND ASSESSMENT GAPS

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ABSTRACT

One important criterion for assessment of POPs/pesticide destruction technologies is the potential formation of new POPs and other toxic by-products. In particular the issue of whether highly toxic polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs) are formed and under which operation conditions their formation is relevant needs to be raised. For incineration processes the formation mechanisms of PCDD/PCDFs have been investigated thoroughly and strategies and technologies have been developed to minimize their formation and emission. A detailed assessment of non-combustion technologies with respect to PCDD/PCDF formation is, however, lacking to date. The comparison of reaction conditions for PCDD/PCDF formation from precursor formation studies and actual applied conditions of a broad range of proposed POPs/pesticide destruction technologies indicates that the operation conditions for a number of destruction technologies have the potential to generate high concentrations of PCDDs/PCDFs if dioxin precursors are present and that also PCDD/PCDF de novo formation can take place. Therefore strategies and regulations for more thorough assessment and monitoring of PCDD/PCDF formation and emission is essential to evaluate POPs/pesticide destruction technologies and for a sound risk management of POPs and obsolete pesticides. The present paper aims to provide a critical impulse in this respect. It discusses the relevant formation pathways of PCDDs/PCDFs with respect to POPs/pesticide destruction technologies and proposes a basic framework on how evaluations should be performed.

Keywords: Dioxin, POPs, reduction, elimination, Pesticides, PCDD, PCDF, destruction, toxicity, Stockholm Convention.

INTRODUCTION

The Stockholm Convention on Persistent Organic Pollutants (POPs) states in Article 6 that POPs waste should be destroyed or disposed of in a way that the POPs content is destroyed or irreversibly transformed. In this context it is critical that the destruction methods used do not create by-products that are themselves POPs (Stockholm Convention 2001). The same criteria should be required for the destruction of obsolete pesticide stockpiles around the globe. Therefore one important criterion (see Table 1) for assessment of POPs/Pesticide destruction technologies is the potential formation of POPs and other toxic by-products, in particular if higher toxic PCDDs/PCDFs are formed and under which operation conditions their formation is relevant (for the respective POPs destruction technology).

To date, a detailed evaluation of PCDD/PCDF emissions has been performed for full-scale facilities only for incineration (the baseline destruction technology for POPs and obsolete pesticides). Within this process the formation mechanisms of PCDD/PCDFs have been investigated thoroughly (Kilgroe et al. 1991, Addink and Olie 1995, Hunsinger et al. 2001, 2003) and strategies and technologies have been developed to minimize their formation and emission (Buekens and Huang 1998; Hagenmaier 1991; Kilgroe et al. 1991).

The discovery of PCDD/PCDF emissions from waste incinerators resulted in difficulties of public acceptance of waste incinerators. A “safe” destruction of hazardous waste (including PCBs and pesticides) demands state-of-the-art hazardous waste incinerators, which are available only in a few countries.

These two challenges led to the development of alternative non-combustion technologies (Rahuman et al. 2000, UNEP 2004) for the destruction of POPs, pesticides, and other hazardous chemicals.

A detailed evaluation of these non-combustion technologies with respect to PCDD/PCDF formation is, however, lacking to date.

A laboratory study of PCB destruction by Super critical water oxidation (SCWO) – a technology listed by NATO/CCMS and United Nations Environmental Programme (UNEP 2004) as “Commercialised Technology with Considerable Experience” – have revealed that considerable amounts of PCDFs can be formed under these conditions, even within temperatures of actual application (Weber 2004a). This highlights the necessity of a more rigorous assessment of non-combustion technologies with respect to their PCDD/PCDF formation potential and their actual applicability for POPs/Pesticide destruction.

The present paper discusses the formation pathways of PCDD/Fs under various conditions of combustion based and non-combustion based technologies proposed for POPs/pesticide destruction. Further, the current knowledge of POP formation during these processes is summarised and critical gaps in the understanding of POP formation are identi-

Table 1: List of criteria for evaluation of POPs/Pesticide destruction technologies (Lodolo 2002)

- Applicability (target contaminants);
- Overall cost;
- Reliability and maintenance;
- Safety;
- Residuals produced (by-products: PCDD/PCDF, other POPs, other toxic compounds);
- Minimum achievable concentration;
- Public acceptability;
- Development status;
- Environmental impacts;
- Performance dependency on site characteristics;
- Clean-up time required;
- Decontaminated soil quality;
- Site data needed
DISCUSSION

1. Formation pathways and conditions of PCDD
PCDF formation (Figure 1)

The formation mechanisms of PCDDs/PCDFs have been investigated during the last two decades in numerous laboratory studies, combustion processes and industrial facilities under various conditions and have been reviewed (Addink and Olie 1995; Ballschmiter and Bacher 1996; Buekens and Huang 1998; Hagenmaier 1991; Kilgroe et al. 1991). Two fundamental PCDD/PCDF formation pathways can be distinguished: the formation via precursor compounds and the formation via the degradation of carbon species in the presence of a chlorine source (de novo synthesis). The evaluation of the potential relevance of these PCDD/PCDF formation pathways for the respective POPs destruction technology is crucial for the assessment of the technology.

1.1 Formation of PCDD/PCDF from precursors

PCDD/PCDF can be formed from most chlorinated aromatic compounds (chlorinated phenols (PxCP) and derivatives, halogenated diphenylethers (PXDEs), polychlorinated biphenyls (PCBs) etc. (Figure 1)). The PCDD/PCDF formation from these precursors can take place even at room temperature, e.g. photochemically by UV/sunlight irradiation (Ballschmiter and Bacher 1996; Choudry and Webster 1987) or enzyme mediated (Ballschmiter and Bacher 1996; Öberg and Rappe 1992). Thermally they can be formed e.g. under basic conditions at low temperatures already around 150°C (Ballschmiter and Bacher 1996). Importantly, several key obsolete pesticides are potent PCDD/PCDF precursors (2,4-D, 2,4,5-T, PCP, CNP, other chlorinated aromatic pesticides). Therefore, this formation pathway is highly relevant to the destruction of obsolete pesticide stockpiles (see below). Furthermore, halogenated precursors can be formed from a broad range of halogenated molecules by elimination reaction already at temperatures below 200°C (depending e.g. on the halogen substitution, presence of metals, specific reaction conditions). For example HCH/Lindane can form chlorinated benzenes by simple elimination steps and PCDD/PCDF were found in the residues of HCH production in the % range (46.5g/kg) (Degler and Uentzelmann 1984). Therefore the precursor formation pathways have to be considered for halogenated pesticides under a wide range of reaction/degradation conditions even if no classic PCDD/PCDF precursors are in the respective POPs/pesticide waste stream (Figure 1).

1.2 PCDDs/PCDFs formation via de novo synthesis (Addink and Olie 1995)

PCDDs/PCDFs can be formed during degradation of unburned carbon species (including PAHs, soot etc.) in the presence of a chlorine source (chlorine, metal chlorides). POPs and pesticide waste often contain a high chlorine content and organic carbon. Therefore, the emission flux from POPs destruction has the basic “material property” for de novo synthesis. De novo synthesis starts at temperatures around 200°C with a maximum formation rate between 300 to 500°C. Therefore this pathway can become relevant for all POPs destruction technologies operating at temperatures above 200°C. From experience gained from incinerators, de novo formation is expected to become particular relevant in the cooling zones of high temperature destruction technologies.

2. Classification of POPs/pesticide destruction technologies and critical points with respect to their potential of PCDD/PCDF formation

POPs and pesticide destruction technologies can be classified into oxidative and reductive destruction processes (Figure 2). Some technologies can be operated under/utilize both conditions (e.g. bio-remediation technologies) or use oxidation only as a supporting degradation power (e.g.
The problematics of PCDD/PCDF formation includes also the technologies operating under pyrolysis conditions (low/no oxygen). Formation of PCDD/PCDF from precursors does not require the presence of oxygen and also de novo formation can take place even in inert atmosphere (Grabic et al. 2000, Laue 1997). In this respect it has been reported that for low temperature pyrolysis processes (450-600°C) with chlorine content of ca. 5% (lower than can be expected for chlorinated POPs/pesticide waste), high PCDD/PCDF concentrations can be generated (up to 10000 mg TEQ/ton waste input) (Weber and Sakurai 1999).

Continuous stable operation of a man-made facility operated by humans is an unattainable aim. One key question for the assessment of POPs destruction technologies therefore is the impact of unstable operation conditions on PCDD/PCDF/POPs emissions and on the total destruction efficiency.

In unstable operating conditions in which temperatures fluctuate, formation routes a) and b) have to be considered, which could result in considerable POPs and PCDD/PCDF emissions even for short term operational disturbances. Therefore one crucial point of assessment of POPs destruction technology is the operation stability, the reaction time to stop POPs feeding when unstable operation conditions occur and the emissions values of POPs under these conditions. The assessment of long term operation stability and resulting average POPs emission cannot be evaluated by short-term sampling but requires continuous sampling of effluent streams. Only continuous monitoring of POPs (including PCDD/PCDF) and other toxic effluents in the effluent streams allows a final way to determine the destruction efficiency of a facility. Up to now the evaluation of all POPs/pesticide destruction technologies and respective destruction efficiencies are based on short-term measurements and are mostly provided by the companies. The meaningfulness of these data are questionable and do not allow any conclusions on long-term operation and a final evaluation of total destruction efficiencies. Finally, destruction efficiencies have to be determined by long term monitoring over weeks and months and should be performed for the whole duration of each POPs destruction project.

2.2 Oxidative non-combustion technologies: (e.g. SCWO, Catalytic Oxidation, Mediated Electrochemical Oxidation (CerOx<sup>TM</sup>, AEA silver IITM), others)

Critical POPs/Pesticides for oxidative destruction are PCDD/PCDF precursors, which only require a condensation step (e.g. chlorophenols and derivatives) or an oxygen insertion (e.g. PCBs) for PCDD/PCDF formation (Figure 1). No comprehensive evaluation has been conducted for any of these technologies in respect to PCDD/PCDF and other POPs formation potential.

A laboratory study demonstrated for one of the oxidative destruction technologies - the SCWO technology - the potential to form tremendous concentrations of PCDF (in the % range); < 7% based on the amount of degraded PCBs) during PCB degradation even at temperatures of practical operation (Weber 2004a). Due to the higher toxic equivalency factors of PCDFs compared to PCBs, the total TEQ of
the reaction mixture increased in almost all the experiments compared to the TEQ of the starting PCB-mixture. The study showed that even for PCB destruction efficiencies of 98.7% or 99.8%, the total TEQ can tremendously increase (by 1000% and 50% respectively) due to PCDD/PCDF formation.

The formation and emission of PCDD/PCDF in combination with corrosion problems and high operation costs resulted recently in the close down a 100 Mio $ wet oxidation process (Knechtl 2001). The operation and maintenance of the facility was performed in full protection clothes and under other protection measures due to PCDD/PCDF contamination.

The SCWO process highlights that PCDD/PCDF formation – precursor formation and de novo formation - is not limited to combustion processes but that so-called non-combustion technologies can face the problem possibly even in a more pronounced manner, which should be evaluated and reflected in the reports on non-combustion technologies of NATO-CCMS, UNEP, and UNIDO.

On the other hand, the catalytic destruction on a TiO₂-Based V₂O₅-WO₃ catalyst demonstrates that PCDD/PCDF formation during destruction of POPs including PCBs can be overcome also by oxidative non-combustion technologies (Weber 2004b). Both studies (Weber 2004a, 2004b) demonstrate that for oxidative destruction technologies the risk of PCDD/PCDF formation has to be assessed with respect to temperature/time dependence of PCDD/PCDF formation. In addition, these studies show that information on temperature and time dependence is inevitable for the evaluation of the applicability of a technology and provides the basis for a risk assessment concerning the relevance of operation stability.

2.3 Reductive technologies (e.g. Base Catalysed Destruction (BCD) Process, APEG, GPCR, Copper Catalysed Dehalogenation, Fly Ash Catalysed Destruction (Hagenmaier Process), Sodium Reduction, Solvated Electron Technology™, others)

A third approach to degrade POPs and pesticides are reductive destruction processes.

2.3.1 Base mediated destruction processes (e.g. Base Catalysed Destruction (BCD); APEG; Ball milling)

It is known that yields of PCDDs in % range can be formed from chlorophenols under alkaline conditions at temperatures as low as 150°C (Ballschmiter and Bacher 1996). In fact, the formation of PCDDs by base mediated processes is the preferred synthesis method of PCDD (Ballschmiter and Bacher 1996; Buser 1975). In addition, high concentrations of PCDFs can be generated from PCBs under alkaline conditions at moderate temperatures (200-300°C) within minutes (Weber et al. 2001). Some base mediated destruction methods operate in this temperature regime (e.g. BCD Process, APEG). This indicates that the critical criteria with respect to the generation of high yields of PCDD/PCDFs is the destruction velocity of the PCDD/PCDF precursors (PCBs, chlorophenols and derivatives) in comparison to the formation rate of PCDD/PCDFs under the respective conditions (and further the degradation rate of the formed PCDD/PCDF). The long residence time e.g. of the BCD process (up to 8 hours) proposes that the destruction velocity is rather low. Therefore the risk of PCDD/PCDF formation seems high for these processes. However no detailed research and sufficient monitoring have been performed.

2.3.2 Non-base mediated metal based dechlorination processes (e.g. Copper Catalysed Dehalogenation; Fly Ash Catalysed Destruction (Hagenmaier Process); Sodium Reduction)

The risk of forming PCDD/PCDFs from precursors seems lower for sodium, copper or fly ash catalysed dechlorination than base mediated processes. However, the fate of condensation reactions has also to be assessed for these technologies in particular for the destruction of precursor containing waste.

2.3.3 Formation of other toxic by-products during reductive processes

A further critical question for all reductive destruction technologies are the final end products of the degradation process. While oxidative technologies strive for the complete mineralization of POPs and pesticides to CO₂, H₂O, HCl etc., the end products of the reductive technologies are less or not defined (Figure 2). In particular for base mediated processes the formation of partially hydroxylated/halogenated organics can be expected. A broad range of hydroxylated PCBs, hydroxylated halogenated aromatics and hydroxylated organics are potent endocrine disrupting chemicals (UBA 1997; Solmsen 1945). The endocrine disrupting potency can even increase by several orders of magnitude by substituting chlorine by hydroxyl groups. For example the endocrine disrupting activity of DDT (1,1,1-Trichloro-2,2-bis (4-chlorophenyl)ethan) (Nelson 1974) increases 10 to 100 times if the chlorine atoms of the phenyl group are substituted by hydroxyl groups (1,1,1-Trichloro-2,2-bis (4-hydroxyphenyl)ethan) (Ousterhout et al. 1981).

A strategy for risk assessment of these waste streams from reductive destruction technologies is therefore pertinent. The chemical complexity of the waste streams requires, in addition to the conventional analytic methods, the support of bioassays for assessment.

In a first step the technology provider have to provide a basic description of “end products” (as is e.g. described for the Gas phase chemical reduction (GPCR) process), detailed analysis of the end products of pilot and full-scale tests and have to allow independent toxicological evaluation of waste streams. The same evaluation is necessary for all destruction technologies if relevant amounts of products of incomplete destruction are produced. Finally, the technology providers have to guarantee detoxification of the waste and not only destruction efficiencies of some target compounds.

CONCLUSIONS

The evaluation of PCDD/PCDF formation is an important criterion for the assessment of POPs/Pesticide destruction technologies. However, to date there is a lack of infor-
mation/assessment for most of the proposed/listed POPs destruction technologies.

Sound evaluations on PCDD/PCDF formation and suppression are currently available only for the high temperature destruction processes of incineration (Buekens and Huang 1998; Hagenmaier 1991; Kilgroz et al. 1991). However, even for these technologies a comprehensive study on POPs destruction efficiencies and total PCDD/PCDF output/ton including long-term operation assessment by continuous monitoring is still missing. For all other POPs destruction technologies even the fate of PCDD/PCDF formation and hence strategies for suppression are unknown. For example, for all other high temperature technologies the fate of PCDD/PCDF formation in the cooling zone is not investigated.

The detailed assessment of PCB destruction by SCWO Processes (Weber 2004a) revealed that high concentrations of PCDD/PCDFs in the % range can be generated by a technology listed as the highest rank of non-combustion technologies from UNEP (UNEP 2004) and UNIDO (Rahuman et al. 2000) and included in the NATO/CCMS list for pesticide remediation. This shows the necessity of a more rigorous assessment of non-combustion technologies with respect to their PCDD/PCDF formation potential and their actual applicability for POPs/pesticide destruction when PCDD/PCDF precursors are in the waste feed.

Furthermore, a comparison of reaction conditions for PCDD/PCDF formation from precursor formation studies and actual applied conditions of a broad range of POPs/pesticide destruction technologies indicates that the operation conditions have the potential to generate high concentrations of PCDDs/PCDFs for a number of destruction technologies if dioxin precursors are present high.

However, an assessment of PCDD/PCDF formation in dependence of operation conditions and stability is missing for most POP/pesticide destruction technologies. The assessment of operation stability and resulting average POPs emission cannot be evaluated by short-term sampling but requests continuous sampling of effluent streams. Continuous monitoring of POPs (including PCDD/PCDF) emission and other toxic effluents in the effluent streams would also allow a final determination of the destruction efficiency of a facility, the comparison of technologies in this respect and a comprehensive risk assessment. The present announced destruction efficiencies are based on short-term measurements and are mostly provided by the companies. The meaningfulness of these “efficiencies” is questionable. Destruction efficiencies and toxicity of effluents should be determined by long term monitoring over weeks and month, measured under supervision of e.g. UN or state authorities or another independent body and should even be requested for the whole duration of a POPs/pesticide destruction project.

Therefore a strategy and regulation for a more profound assessment of the fate of PCDD/PCDF formation is essential for the evaluation of POP/pesticide destruction technologies and for a sound risk management of POPs and obsolete pesticide stockpiles. This may include the following items:

Step 1: Laboratory and pilot plant evaluation of conditions for safe destruction and conditions associated with PCDD/PCDF formation (and other toxic emissions) for the respective technology. The studies of PCB destruction over TiO2-Based V2O5-WO3 catalyst (Weber 2004b) and PCB destruction in SCWO (Weber 2004a) may serve as one example in this respect for laboratory studies.

Step 2: Assessment of reliability/stability of long term operation conditions and the fate of irregular operation (e.g. non-stationary conditions, start-up, shut-down). Up until now this has only been evaluated for high temperature incineration. The assessment and compliance of operation stability has to be demonstrated in the pilot plant phase and continuously monitored and documented for full-scale facilities.

Step 3: Monitoring and supervision of destruction efficiencies and toxic emissions from pilot and full-scale operations of POPs destruction processes. The assessment has to include toxicity considerations and requests the monitoring of PCDDs/PCDFs and total toxicity (TEQ; other toxicity criteria, bio assays). For the assessment all waste streams should be including in the monitoring to assess the total destruction efficiency (based on toxicity). Finally, the responsible company have to guarantee the detoxification of the waste and not only destruction efficiencies of some target compounds.

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THE APPLICATION OF COPPER MEDIATED DESTRUCTION METHOD (CMD) FOR DESTRUCTION OF CHLORINATED PESTICIDES AND SOME PRE-DIOXIN AND POP COMPOUNDS

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ABSTRACT
The principles and experimental parameters of the copper mediated destruction method (CMD) are presented. The dehalogenation pathways of pre-dioxin compounds such as hexachlorobenzene and chlorinated phenols are outlined and experimental results compared with thermodynamic calculations. Similar dechlorination studies were performed with decachlorobiphenyl. The dihedral angles between aromatic rings were calculated and discussed in relation to toxic properties. A special attention was paid to differences between ortho and nonortho isomers. The destruction ability of the CMD method is demonstrated on DDT, hexachlorocyclohexane (Lindane), the mixtures of Lindane with DDT (Gamadyn) and on the samples of the area highly contaminated with PCDD/Fs, PCBs, HCBz, HCH and DDT and its metabolites.

INTRODUCTION
The results obtained in the detoxification of persistent organic compounds, especially hexachlorobenzene (HCBz), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) with the use of a new copper mediated destruction method (1) were presented at international conferences in Prague and Brno (2,3). It was stated that de novo synthetic and dehalogenation reactions are opposite sides of the same process in which the former reaction proceeds in the oxidation and the latter in the oxygen deficient or inert atmosphere. The course of these reactions is connected with the presence of copper in the reaction system. Very good results were received for the destruction of the above mentioned compounds in non-continuous as well as semicontinuous arrangements. In these cases a toluene-extracted fly ash was used as a convenient matrix for detoxification studies.

The present contribution is focused on pre-dioxin compounds detoxification and the applicability of the CMD method to the destruction of chlorinated pesticides.

APPARATUS AND EXPERIMENTAL CONDITIONS
Basic dechlorination experiments were performed under laboratory conditions in the closed, non-mixed ampoule systems. The efficiency of the destruction of studied compounds was also followed in a noncontinuous, efficiently mixed semi-pilot destruction apparatus with the inlet capacity of 25 to 50 kg.

Destruction experiments were performed under the following conditions: reaction temperature 250-300 °C, reaction time 2-4 h, oxygen deficient atmosphere, practically
atmospheric pressure, and the content of copper to the contaminated matter = 1-4 wt. %. The copper amount depended on the concentration of toxic compounds in the reaction system. The destructions were performed both with a matrix (20 kg of the given matrix + ca 10-15 kg of the toxic matter) and without its addition.

RESULTS AND DISCUSSIONS

Mechanism

It is generally accepted that the Ullman reaction can be schematically depicted by the following reaction, where ArCu is an aromatic reaction intermediate:

\[ \text{Ar} X + 2\text{Cu} \rightarrow \text{[ArCu]} + \text{CuX} \]

The present method (CMD) is based on the adjustment of such experimental conditions that ensure selective dehalogenations as the predominant process while potential coupling reactions are efficiently suppressed. It is generally agreed that Ullman reaction proceeds via an arylcopper intermediate, the formation of which likely involves a single electron transfer. However, the exact mechanism of these reactions has not yet been satisfactorily solved.

Dechlorination of pre-dioxin compounds

Pre-dioxin compounds are the main components from which PCDD and PCDF are formed by de novo synthetic reactions. However, compared to the PCDD and PCDF formed, these compounds are present in studied systems in much higher concentrations. Therefore, the effective destruction of these precursors before their coupling might be taken as the important factor in the control of de novo synthetic reactions determining the extent of PCDD and PCDF formation.

Hexachlorobenzene dechlorination

Literature data show that the o-chlorine positions of the compound are most favorable sites for the coupling reactions. The full dechlorination to benzene (4) was easily affected by the CMD method under given experimental conditions. The step dechlorination follows the main pathway: hexachlorobenzene > pentachlorobenzene > 1,2,3,5 tetrachlorobenzene > 1,3,5 trichlorobenzene > 1,3 dichlorobenzene > monochlorobenzene > benzene which agrees with thermodynamic calculations. The o-chlorines are preferential dehalogenation sites. From the thermodynamics studies it follows that copper in the solid phase does not function as the true catalyst but acts as one of the reaction components.

Pentachlorophenol dechlorination

It is well known that chlorinated phenols readily undergo coupling reactions to produce PCDF and PCDD, especially when the chlorine is in the o-position. We have found (5) that the dechlorination C-Cl bond activity sharply decreases along the sequence: ortho > para > meta with respect to the OH group. However, even in the cases where chlorinated phenols were fully dechlorinated by the CMD method, the coupling reactions proceeded to some extent in the dechlorination system as well. However, PCDD and PCDF were formed in the concentrations approximately three orders of magnitude lower compared to the dechlorinated chlorophenols. Practically the same conclusion as made above for chlorobenzene destructions can be drawn from thermodynamic calculations for chlorophenol reaction systems.

Chlorinated biphenyls dechlorination

Chlorinated biphenyls can under convenient conditions function also as precursors of PCDD and PCDF. The results of experimental dechlorination and thermodynamic calculations (6) lead to the following conclusions:

From the calculations it follows that all chlorinated biphenyls are coplanar (dihedral angle \( \omega \) of biphenyl is 47.3°). The most toxic biphenyls are 3,3',4,4',5 and 3,3',4,4',5,5' - chlorinated isomers. From these calculations it is further evident that these compounds have the same \( \omega \) as the parent biphenyl.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Ballschmitter No.</th>
<th>I-TEF</th>
<th>Dihedral angle ( \omega ) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,3',4,4',5</td>
<td>126</td>
<td>0.1</td>
<td>47.3</td>
</tr>
<tr>
<td>3,3',4,4',5,5'</td>
<td>169</td>
<td>0.01</td>
<td>47.3</td>
</tr>
</tbody>
</table>

The most toxic biphenyls belong to the group of non-ortho chlorinated compounds. The other biphenyls with very low toxicity as demonstrated by their I-TEF values ranging from 0.0005 to 0.00001 belong to the steric non-ortho and mono-ortho chlorine configurations with the dihedral angle ranging from 47.0 to 56.7°. The dihedral angle of nontoxic isomers containing di-ortho (2,6-; 2',6'-), tri-ortho (2,2',6-; 2,2',6'-) and tetra-ortho (2,2',6,6'-) chlorine configurations approaches the value of \( \omega = 90 \)° which means that aromatic rings are practically in perpendicular positions to each other. Under these steric conditions the chlorinated biphenyls can never be toxic. It was proved that the dehalogenation proceeds easily with the chlorines in 3,3',4,4' and 5,5' positions (see the outer sides from the dotted line). On the other hand, the thermodynamic stability towards dechlorination of the isomers with chlorines in di-ortho-, tri-ortho, and tetra-ortho positions is much greater. It should be stressed that under the experimental conditions chosen even these most stable chlorines undergo dechlorination by the CMD method giving biphenyl as the only dehalogenation product.

Dechlorination of chlorinated pesticides

The most frequently applied pesticides in the former Czechoslovakia were Lindane and DDT. In 1981 the consumption of pesticides in the agriculture was approximately 24000 t per ca. 5 mil hectares, i.e. ca 5 kg yearly contamination per ha.

DDT (p,p'-DDT) and its metabolites, DDD and DDE, have the following composition,

where A denotes the following chlorinated groups:
However, also o,p′-DDT, o,p′-DDD and o,p′-DDE are formed as the minor components during p,p′-DDT production. Under environmental conditions p,p′-DDT is slowly dehydrochlorinated to p,p′-DDE with the half time of ca 8-15 years. The destruction of these compounds by the CMD method proceeds via the molecule disruption, affording dechlorinated benzene, trichloromethane and lower chlorinated hydrocarbons among other dechlorination products. Although the C-Cl bond cleavage proceeds practically quantitatively, the dechlorination efficiency for the chlorinated A-species, if it exists at all, is difficult to judge.

The very efficient insecticide, hexachlorocyclohexane (HCH, Lindane), was also produced in the former Czechoslovakia by benzene chlorination and consisted of the four stereoisomers. The most effective insecticidal isomer is α-HCH. The CMD method seems convenient also for the destruction of hexachlorocyclohexanes even though these compounds are not aromatic. Unfortunately, any conclusions as to the course of the dehalogenation process are difficult to make from the analytical results because of the volatility of the products. We believe that the ring disruption cannot be excluded.

**Results of dechlorination experiments**

1. The destruction of Lindane and DDT from the contaminated floor in Luby (Czech Republic). Experimental conditions: without matrix, 300 °C, 4 h, the copper amount to the contaminated matter = 2 wt.%. The results are presented in Table 1. Lindane was destroyed from 99.2% and hexachlorobenzene and DDT underwent total destruction.

2. The destruction of Gamadyn (mixture of DDT and Lindane) which is a Czech commercially produced insecticide. Experimental conditions: matrix-extracted fly ash (25 kg) + Gamadyn (10 kg), the copper amount to the contaminated matrix = 4 wt.%. The results are presented in Table 2. DDT and Lindane underwent total destruction.

3. The destruction of PCDD, PCDF, PCB, chlorobenzenes and pesticides in contaminated floor samples of the Czech Republic.

### Table 1. Destruction of lindane and DDT

<table>
<thead>
<tr>
<th>Compound</th>
<th>before destruction</th>
<th>after destruction</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-HCH</td>
<td>80 ng/g</td>
<td>&lt;1.5</td>
</tr>
<tr>
<td>β-HCH</td>
<td>56 ng/g</td>
<td>&lt;2.1</td>
</tr>
<tr>
<td>γ-HCH</td>
<td>5340 ng/g</td>
<td>4.5</td>
</tr>
<tr>
<td>δ-HCH</td>
<td>38 ng/g</td>
<td>&lt;2.5</td>
</tr>
<tr>
<td>HCB</td>
<td>43 ng/g</td>
<td>&lt;0.6</td>
</tr>
<tr>
<td>p,p′-DDE</td>
<td>385 ng/g</td>
<td>&lt;1.1</td>
</tr>
<tr>
<td>p,p′-DDD</td>
<td>2760 ng/g</td>
<td>&lt;1.4</td>
</tr>
<tr>
<td>p,p′-DDT</td>
<td>183 ng/g</td>
<td>&lt;1.9</td>
</tr>
<tr>
<td>p′,p′-DDD</td>
<td>175 ng/g</td>
<td>&lt;1.9</td>
</tr>
<tr>
<td>p′,p′-DDT</td>
<td>4040 ng/g</td>
<td>&lt;2.4</td>
</tr>
<tr>
<td>p,p′-DDE</td>
<td>2630 ng/g</td>
<td>&lt;6.6</td>
</tr>
<tr>
<td>p,p′-DDD+op DD T</td>
<td>5514 ng/g</td>
<td>4.5</td>
</tr>
<tr>
<td>HCB</td>
<td>43 ng/g</td>
<td>BLOQ</td>
</tr>
<tr>
<td>Σ DDT</td>
<td>10173 ng/g</td>
<td>BLOQ</td>
</tr>
<tr>
<td>Σ OCP</td>
<td>15730 ng/g</td>
<td>4.5</td>
</tr>
</tbody>
</table>

BLOQ - below limit of quantitation

### Table 2. Destruction of Gamadyn

<table>
<thead>
<tr>
<th>Compound</th>
<th>before destruction</th>
<th>after destruction</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-HCH</td>
<td>2910 µg/g</td>
<td>&lt;0.0033</td>
</tr>
<tr>
<td>p,p′-DDE</td>
<td>530 µg/g</td>
<td>&lt;0.015</td>
</tr>
<tr>
<td>p,p′-DDD+op DD T</td>
<td>5320 µg/g</td>
<td>&lt;0.023</td>
</tr>
<tr>
<td>p,p′-DDT</td>
<td>689000 µg/g</td>
<td>&lt;0.0095</td>
</tr>
<tr>
<td>Σ OCP</td>
<td>77660 µg/g</td>
<td>&lt;0.051</td>
</tr>
</tbody>
</table>

BLOQ - below limit of quantitation

### Table 3. Destruction of PCDD/F-contaminated floor

<table>
<thead>
<tr>
<th>Compound</th>
<th>before destruction</th>
<th>after destruction</th>
</tr>
</thead>
<tbody>
<tr>
<td>2378 TCDD</td>
<td>1760 ng/g</td>
<td>0.588</td>
</tr>
<tr>
<td>12378 PeCDD</td>
<td>4.63 ng/g</td>
<td>&lt;0.11</td>
</tr>
<tr>
<td>123478 HxCDD</td>
<td>1.87 ng/g</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td>123678 HxCDD</td>
<td>0.782 ng/g</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>123789 HxCDD</td>
<td>0.315 ng/g</td>
<td>&lt;0.099</td>
</tr>
<tr>
<td>1234678 HpqCDD</td>
<td>94.4 ng/g</td>
<td>&lt;0.41</td>
</tr>
<tr>
<td>OqCDD</td>
<td>9390 ng/g</td>
<td>&lt;0.91</td>
</tr>
<tr>
<td>TCDD</td>
<td>2010 ng/g</td>
<td>1.14</td>
</tr>
<tr>
<td>PeCDD</td>
<td>19.2 ng/g</td>
<td>0.639</td>
</tr>
<tr>
<td>HxCDD</td>
<td>11.8 ng/g</td>
<td>0.873</td>
</tr>
<tr>
<td>HpqCDD</td>
<td>204 ng/g</td>
<td>&lt;1.4</td>
</tr>
<tr>
<td>Σ PCDD</td>
<td>11635 ng/g</td>
<td>2.5</td>
</tr>
<tr>
<td>Σ 1-TEQ PCDD</td>
<td>1767 ng/g</td>
<td>0.665</td>
</tr>
<tr>
<td>2378 TeCDF</td>
<td>3.27 ng/g</td>
<td>&lt;0.065</td>
</tr>
<tr>
<td>12378 PeCDD</td>
<td>3.82 ng/g</td>
<td>&lt;0.085</td>
</tr>
<tr>
<td>23478 PeCDD</td>
<td>5.26 ng/g</td>
<td>&lt;0.065</td>
</tr>
<tr>
<td>123478 HxCDF</td>
<td>139 ng/g</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td>123678 HxCDF</td>
<td>723 ng/g</td>
<td>&lt;0.13</td>
</tr>
<tr>
<td>234678 HxCDF</td>
<td>3.86 ng/g</td>
<td>&lt;0.17</td>
</tr>
<tr>
<td>123789 HxCDF</td>
<td>1.23 ng/g</td>
<td>&lt;0.19</td>
</tr>
<tr>
<td>1234678 HpqCDF</td>
<td>30.5 ng/g</td>
<td>&lt;0.17</td>
</tr>
<tr>
<td>1234789 HpqCDF</td>
<td>12.2 ng/g</td>
<td>&lt;0.36</td>
</tr>
<tr>
<td>OCDF</td>
<td>330 ng/g</td>
<td>&lt;0.91</td>
</tr>
<tr>
<td>TCDF</td>
<td>144 ng/g</td>
<td>&lt;0.32</td>
</tr>
<tr>
<td>PeCDD</td>
<td>76.2 ng/g</td>
<td>&lt;0.43</td>
</tr>
<tr>
<td>HxCDF</td>
<td>1130 ng/g</td>
<td>&lt;0.69</td>
</tr>
<tr>
<td>HpqCDF</td>
<td>103 ng/g</td>
<td>&lt;0.89</td>
</tr>
<tr>
<td>Σ PCDF</td>
<td>1783 ng/g</td>
<td>BLOQ</td>
</tr>
<tr>
<td>Σ 1-TEQ PCDF</td>
<td>90.3 ng/g</td>
<td>0.0588</td>
</tr>
<tr>
<td>Σ PCDD/F</td>
<td>13418 ng/g</td>
<td>2.5</td>
</tr>
<tr>
<td>Σ 1-TEQ PCDD/F</td>
<td>1857 ng/g</td>
<td>0.72</td>
</tr>
</tbody>
</table>

BLOQ - below limit of quantitation

### Table 4: Destruction of PCB-contaminated floor

<table>
<thead>
<tr>
<th>Compound</th>
<th>before destruction</th>
<th>after destruction</th>
</tr>
</thead>
<tbody>
<tr>
<td>TriCB</td>
<td>803 ng/g</td>
<td>3.7</td>
</tr>
<tr>
<td>TetrCB</td>
<td>3059 ng/g</td>
<td>6.0</td>
</tr>
<tr>
<td>PentCB</td>
<td>13862 ng/g</td>
<td>11.1</td>
</tr>
<tr>
<td>HexaCB</td>
<td>108785 ng/g</td>
<td>36.6</td>
</tr>
<tr>
<td>HeptaCB</td>
<td>46994 ng/g</td>
<td>19.4</td>
</tr>
<tr>
<td>OctaCB</td>
<td>15570 ng/g</td>
<td>5.2</td>
</tr>
<tr>
<td>NonaCB</td>
<td>1607 ng/g</td>
<td>0.00</td>
</tr>
<tr>
<td>DekaCB</td>
<td>3691 ng/g</td>
<td>0.70</td>
</tr>
<tr>
<td>Σ PCB</td>
<td>194371 ng/g</td>
<td>83</td>
</tr>
</tbody>
</table>

NA- not analyzed

### Table 5: Destruction of PCBz-contaminated floor

<table>
<thead>
<tr>
<th>Compound</th>
<th>before destruction</th>
<th>after destruction</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCDF</td>
<td>1190 ng/g</td>
<td>&lt;1.4</td>
</tr>
<tr>
<td>TCDF</td>
<td>13862 ng/g</td>
<td>&lt;0.15</td>
</tr>
<tr>
<td>PeCDD</td>
<td>150 ng/g</td>
<td>&lt;0.60</td>
</tr>
<tr>
<td>HxCDF</td>
<td>49194 ng/g</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td>OctaCB</td>
<td>15570 ng/g</td>
<td>&lt;0.13</td>
</tr>
<tr>
<td>NonaCB</td>
<td>1607 ng/g</td>
<td>&lt;0.40</td>
</tr>
<tr>
<td>DekaCB</td>
<td>3691 ng/g</td>
<td>&lt;1.5</td>
</tr>
<tr>
<td>Σ PCB</td>
<td>194371 ng/g</td>
<td>&lt;0.69</td>
</tr>
</tbody>
</table>

NA- not analyzed

BLOQ - below limit of quantitation
and delta) and 15460 ng/g of DDT and its metabolites. HCH was destroyed from 99.998% and DDT was below the limit of quantisation.

REFERENCES

(2) Pekárek V. Scientific activities of the Dioxin Laboratory at ICPF. PREWIN GS and GA, Prague, Czech Republic, 14th-16th May 2003. 
Fe-TAML/H2O2 System Features
• Rapid acting and safe - for people and environment
• Catalytic – Requires very low catalyst and relatively low peroxide concentration
• Designed to be Non-toxic – No toxic elements or functionalities
• Aqueous based – Compatible with wide variety of surfaces and technologies; can be used on sensitive equipment
• Broad-spectrum activity – Detoxify and degrade large range of chemicals and inactivate bacterial spores
• Performance previously unavailable – Truly biomimetic with deep oxidation capability (leaves no toxic byproducts)
• Robust system – Stable and functional over wide range of pH
• Easy to use – Used at ambient conditions, offers a practical approach.

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Undergraduate Students: Mheta Akin; Darin Flynn; Cheryl Hendricks; Sherry Mayer; Anna Melnichuk; Douglas Mitchell; Christopher Noser; Duane Prasuhn; Victor Polshin; Yong-Li Qian; Brad Steinhoff; Erin Upham

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OTA, Massachusetts - Paul Richard; Dr. Augustus Oganbameru
NETL, DOE, Pittsburgh - Dr. Anthony Cugini; Dr. Bret Howard; Dirk D. Link
Forest Res. Inst., NZ - Dr. Trevor Stuthridge; Murray J. Robinson
US Naval Surface Warfare Center - Jerry Brown
Univ. Louisiana, Monroe - Prof. Richard Norman
Osaka City University - Prof. Isamu Kinoshita, Hideaki Takagi; Toshihiro Yano

Degradation of Pentachlorophenol (PCP)
Reaction Conditions
• pH 10, carbonate buffer – used to dissolve PCP
• 25 °C, 9 minutes reaction time – quench with HCl
• 9 equivalents of H2O2 stoichiometric for complete mineralization.

INTRODUCTION

The base catalysed degradation (BCD) technology is one of the very few non incineration technologies for destroying POPs which have been commercialised. Indeed, since the BCD process treats not only POPs waste but also POP’s contaminated soil it has by far the most extensive track record.

The process has been presented at previous HCH conferences, where the chemistry and applications in projects such as the treatment of HCH waste in the Basque country were explained in detail.

The BCD process was developed by the US-EPA in a programme to find alternatives to incineration for such chlorinated contaminants as PCB’s. The EPA however developed only the chemistry of the process and proved the destruction of chlorinated organic species, without the formation of undesirable breakdown products on a laboratory scale. Development into an industrial scale process was left to the licensees of the process.

Usually the development was undertaken by small, undercapitalised companies or developed only as far as to be useful for a single remediation project.

LESSONS LEARNED FROM PREVIOUS PROJECTS

Many of the large scale soil remediation projects in the USA used the BCD chemistry to treat only proportionately small quantities of dust and condensate in which the POP’s were concentrated. Effort was concentrated on treating the very large soil volumes as efficiently as possible. Little effort was expended on the much smaller scale reaction activities to destroy the POPs removed from the soil, other than to ensure their complete destruction.

The process, in combination with soil treatment was used at the Olympic site in Sydney, Australia to treat the concentrated, extracted POPs as well as pure HCB and PCT wastes. An attempt was made to change the reactor design to increase the speed of reaction and improve reactor productivity. Previously in Australia there had been considerable effort to find catalysts which were more effective than the carbon catalyst proposed originally by the US-EPA. This work had been successful and lead to operations which were able to destroy all tested species of chlorinated organics to below detection limit, irrespective of the amount of chlorine within the molecule. Those companies using the old catalyst on simple jobs still state that there is a limit of say 10% chlorine above which the process is ineffective. This is completely erroneous, as has been demonstrated on a daily basis with tonnes upon tonnes of HCH and HCB waste as well as pure PCB’s.

The attempt to improve the reactor by means of a heated pump around circuit in contrast to the simple electrically heated reactors used previously was not successful. This principle, employed in many applications such as oil refining was not suitable for the more complex mixture of liquid, semi-plastic and solid phases encountered in the BCD reaction. The failed efforts to bring this system into operation and the eventual costs of reverting to the original reactor design resulted in disproportional costs for the project which were not differentiated in overall cost figures.

A survey of non incineration processes performed on behalf of the Danish Environmental Ministry was given raw, un-differentiated facts and as such presented costs for the process which do not reflect the true situation. Due to the time lost, the Olympic project was then carried out in haste, without any attempt to reduce the consumption of chemicals. Again this was reflected in the above mentioned study.

Even when such projects go wrong they can be useful in that they very clearly highlight areas needing improvement. With detailed information from the Olympic project we took the opportunity to further develop the process as part of and a new project. This is the remediation of a very complex environmental problem at a chlorine based chemicals factory in the Czech Republic. This project will remediate a site used previously for the conversion of HCH waste to TCB, and other, not always specified pesticides production activities.

The site is characterised by very high dioxin contamination as well as large quantities of HCH and HCB, both as soil contaminants and as pure waste. The old production buildings are themselves very contaminated, and still include all the old equipment, piping, electrical systems etc. left unchanged and further corroded from the day, about 40 years ago when they were shut down without any decommissioning. The surrounding soil area has become heavily contaminated from leaking storage tanks and waste solid chemicals simply stored outside. These old production buildings are on the edge of the factory adjacent to residential areas.

TARGETED IMPROVEMENTS

Criticism levelled at the process included not only the high cost of the destruction reaction, mentioned before, but also the fact that the reagents remaining after the destruction reaction, although non toxic are still a waste and represent a volume sometimes more than double the original waste quantity. Again this latter point was not previously highlighted since most large operations had been within soil remediation projects, and this waste represented only a small fraction of the treated soil.

We listed the improvements we wished to make:
1) Reduce overall time of the reaction and improve reactor productivity
2) Reduce requirement for excess NaOH in the reaction
3) Reduce process oil consumption
4) Reduce the amount of disposable waste
5) Reduce overall costs
6) Reduce fire risk and overall safety and operational hygiene
7) Reduce analysis costs
8) Improve flexibility of plant and ability to deal with future requirements
**DESIGN CHANGES**

It was possible to group together cause and effect of various shortcomings in the process as it had been practised in the past.

Reactivity, overall reaction batch times and excess reagents were linked primarily to the problem of heating the reactor. Initial work 10 years ago had been made with small pilot reactors of 200 l working capacity using electrical coil heating of the reactor shell. This was cheap and convenient for the task at the time. However, scaling up in this manner leads to ever worsening ratios of available heating surface to volume to be heated. Based on further pilot testing we retained the idea of a self contained reactor, but substituted heat transfer oil for the electrical coil heating.

By optimising the stirring of the reactor and primarily the design of the heating coils and thermo-oil system we obtained very favourable heat transfer rates. With this it was no longer a problem to reach the required reaction temperature in a short time and to maintain this temperature when adding reagents. The poor heating rates of earlier designs were in the past compensated by adding excess NaOH. Now this was no longer necessary so that we can operate very close to the stoichiometric ratio of NaOH to bonding chlorine.

By this change targets (1) & (2) were achieved.

In addition it was possible to cool the reactor after completion of the reaction with the very same heat transfer oil, merely by circulating this through a cooled exchanger instead of a fired heater. In the past the reactor was emptied hot and cooling achieved in a dump tank. The only record of a serious accident in a BCD plant was when this was performed without adequate safeguards, which led to a spontaneous fire. By the means now chosen the only point in the whole plant where the donor oil is above its flash point is in the reactor during reaction. Hence part of target (6) was also achieved.

The original concept of the BCD process from the US-EPA was to use a cheap heavy fuel oil as the hydrogen donor. At the end of the reaction, this oil would contain salt and carbon from the decomposition reaction and some excess NaOH. This was then disposed of as fuel in a furnace, cement kiln or similar. It is debatable whether incinerating salt with oil can be an environmental hazard or not. We took the attitude that it should be avoided if possible. Separation of the reaction products from heavy fuel oil at the end of the reaction is not a practical proposition due to the high boiling point and high viscosity of this cheap oil.

Instead we have selected a refined oil with the right chemical properties for the reaction and good physical properties to allow separation. The cost of this oil dictates separation and recycling of the oil after the reaction. After the reaction and cooling, the oil and the solids are separated in a centrifuge. The oil is recycled to the reactor. The remaining sludge of salt, carbon and any mineral solids present still contains roughly its own weight of oil. This is distilled off in a simple electric batch furnace, and the oil recovered as condensate and again returned to the reactor. The remaining salt cake can be further heated to as high as 700°C.

Targets (3), (4) & (5) have been achieved by these means. More than 90% of the oil is recycled. Some oil is unavoidably consumed chemically in the process and small amounts are disposed of as fuel when the flash point, reduced by the thermal cracking reactions taking place, is below a set value. The salt cake, completely free of POPs is disposed of to a controlled landfill, such as would accept salt from flue gas scrubbing processes. The quantity of the salt cake is stoichiometrically dependent on the waste being treated and salt produced. The chlorine has to go somewhere!

In previous projects each batch was analysed before disposal, or where possible before emptying the reactor. This is both costly, especially if dioxin analysis is required and significantly reduces the productivity of the plant. Due to the fact that most of the oil is recycled the number of analyses required is drastically diminished, and it is no longer necessary to hold the reactor until the results become available, thus reducing the operational costs significantly.

The general operational hygiene was improved by enclosing feed preparation and dosing to the reactor so that workers no longer directly handle the waste. This point becomes most important when the waste contains dioxins.

To improve our future flexibility we designed the plant for our present project as 2 separate, fully independent lines. The capacity we require for this particular project is determined by the large amount of dust recovered from the thermal process section for soil treatment and in which the contaminants are concentrated. Future projects are not expected to require such a high capacity. Hence it will be possible to re-locate these 2 lines to 2 separate locations as required.

**SUMMARY**

By analysing the causes and effects of identified weaknesses in the process technology and constructing a pilot plant, designed to remedy the principal causes it was possible to so modify the process that operating costs are now in line with incineration costs. The process has an environmental impact orders of magnitude lower than incineration. Plant can be tailored to reflect the specific details of a job, re-located to site to treat pure POPs wastes or to supplement a soil remediation job with low capital expenditure and can be removed after completion of the task. We are of the opinion that the BCD process now offers a much more effective alternative to incineration, especially where hazardous waste incinerators do not exist, are unable to treat large quantities of pure POPs waste or are unacceptable to the local public.
GPCR TECHNOLOGY AND VENDOR UPDATE

Craig McEwen, Dr. Douglas Hallett, Kelvin Campbell
Hallett Environmental and Technology Group Inc.

ABSTRACT
Gas Phase Chemical Reduction (GPCR) is a proven technology and is well suited for the destruction of Persistent Organic Pollutants such as pesticides. Over the last two years several process improvements have been made to improve the overall operational efficiency and to reduce the utility consumption. Process improvements include increased automation and the addition of a system to recover excess hydrogen from the product gas produced by the process. The recovered hydrogen can be reused and the remaining product gas has characteristics that are better suited for process heating. The addition of the hydrogen recovery system reduces the overall hydrogen consumption of the process by approximately two thirds. Design improvements have also been made to increase the modularity of the equipment. This results in the simplification of the transportation, assembly, and commissioning of the system on site.

Dr. Douglas Hallett invented the application of GPCR technology to the destruction of hazardous organic chemicals in 1986. Dr. Hallett formed ELI Eco Logic International Inc. and brought together a team of engineers and scientists to develop and commercialize the process. The public company that was later formed operated plants in Canada and Australia. In 1998, Dr. Hallett left Eco Logic and formed an environmental consulting firm. The patent rights for GPCR were assigned to Eco Logic, and Eco Logic continued to develop and improve the technology. In 2004, Eco Logic ceased operations. The original inventors and developers of the GPCR technology now work for Hallett Environmental and are dedicated to the continued use of GPCR for the destruction of hazardous organic chemicals.

INTRODUCTION
Hydrogen reduction is well known and is widely used in the chemical industry. The most common usage is in the petroleum industry where it is used to fractionate crude oil to produce gasoline, diesel, heating oil, and other hydrocarbon products. Dr. Douglas Hallett, Royal Dutch/Shell from the Netherlands, and BASF from Germany were among the first to apply for patents using hydrogen reduction to destroy hazardous wastes under specific conditions. During the late 1980s and early 1990s, Dr. Hallett and engineer Kelvin Campbell were granted numerous patents worldwide for the basic process and various process applications. This technology later became known as Gas Phase Chemical Reduction or GPCR.

In 1990, Craig McEwen joined Eco Logic to work with Hallett and Campbell in the development of the process. Mr. McEwen played a lead role in the engineering and implementation of the GPCR technology, and when Eco Logic ceased operations in 2004, he had been the Chief Engineer at Eco Logic for several years. This paper presents recent technology improvements that were developed while Mr. McEwen was at Eco Logic.

GPCR TECHNOLOGY BACKGROUND
Gas Phase Chemical Reduction (GPCR) is a proven technology for the destruction of hazardous organic chemicals and has been successfully applied to PCBs, CFCs, pesticides and chemical warfare agents. The simplified chemical reactions for the destruction of Organochlorines are given below:

\[
\text{Chlorinated Hydrocarbons} + \text{H}_2 + \text{Heat} \Rightarrow \text{CH}_4 + \text{Bz} + \text{HCl}
\]

\[
\text{CH}_4 + \text{Bz} + \text{H}_2\text{O} + \text{Heat} \Rightarrow \text{CO} + \text{CO}_2 + \text{H}_2
\]

Similar reactions can be written for the destruction of fluorinated, brominated, and phosphinated hydrocarbons. The first reaction is the destruction reaction. The second reaction happens to a lesser extent but is important because the addition of water supplies hydrogen to the process. Water is also important because it aids in heat transfer and prevents the formation of carbon particulate.

The process was originally tested at Hamilton Harbour in Ontario, Canada for Environment Canada and further testing was completed at Bay City, Michigan, USA for the United States Environmental Protection Agency. The USEPA testing was done using PCB oil and PCB contaminated soil. In all tests, greater than 99.9999% destruction efficiency was achieved. Based on these successful demonstration projects, commercial scale plants were built and operated in St. Catharines, Ontario, Canada, and in Kwinana, Western Australia. The St. Catharines plant was used to destroy PCBs in transformers and capacitors for General Motors and was successful in making the GM plant PCB free. The Kwinana plant was operated in partnership with Environmental Solutions Inc. and was used to treat similar PCB wastes and was also used to destroy a large stockpile of obsolete DDT pesticide. More recent testing conducted by the US Army successfully demonstrated the ability of the GPCR process to destroy chemical warfare agents such as GB and VX.

In total, the GPCR technology has operated for more than 30,000 hours and has been used to destroy more than 3,000 tonnes of high strength organic wastes. The GPCR technology has always been a technical success, but financial success was not achieved until 1998 and the last two years of operation at the Kwinana plant in Australia.

TECHNICAL ISSUES AND SOLUTIONS

Black Tarry Material
The GPCR technology has always been successful in destroying hazardous wastes but early operations produced a tarry intermediate compound that was formed in the reactor. This material severely limited the process throughput and required frequent maintenance to change filter bags and clean tanks and piping. The input material was destroyed with greater than 99.9999% efficiency but the limitations in throughput made the process expensive to operate.
The issue of black tarry material production is solved. A research project determined that insufficient mixing of the hydrogen with the waste material caused the formation. This was proven at Kwinana in 1999 with the added step of preheating the liquid waste input to its vapour phase but below destruction temperatures. In the vapour phase it was mixed with hydrogen and steam and then this mixture was introduced into the reactor for destruction. Waste preheating and mixing prior to the reactor greatly reduced the formation of tarry intermediates and allowed the process to operate profitably. Recent laboratory-scale testing showed that increasing the steam content even further results in an even greater reduction in carbon and tar formation.

Safety and Complexity

The GPCR technology has an excellent safety record but some people perceive the technology to be unsafe because of the use of hydrogen. The safe use of hydrogen is well known and understood, and hydrogen is a common reactant used in the chemical industry. Many countries and companies are promoting a hydrogen economy and in the future hydrogen will be used to power everything from homes and automobiles to laptop computers and cell phones. Using hydrogen to destroy hazardous waste is no more dangerous than using natural gas in an incinerator. The redundant safety systems used in the GPCR process are based on established engineering guidelines and they do not make the process complex or difficult to operate.

The GPCR technology is robust and simple to operate but some people perceive the technology to be complex. In the operation of the first commercial scale plants, many of the parameters were controlled manually by skilled operators. This allowed fine-tuning of the process parameters on a continual basis because the optimum operational efficiency was not yet established. Many design improvements were incorporated and after each improvement, the optimum operational parameters would change. In recent years, the best operational strategy and parameters have been established and increased automation of the process has been incorporated. From the operator’s point of view the system is now easy to operate because the actual control of the system occurs seamlessly in the background.

COST SAVING OPPORTUNITIES

Modular Design

A new modular design was developed for the United Nations Industrial Development Organisation (UNIDO) project in Slovakia. Most of the process equipment is built into ISO shipping container frames with a minimal number of connections between containers. All stairs, deck- ing, and handrails required are also incorporated into the containers. This design philosophy will allow the unit to be fully built, commissioned and tested before it is delivered to the customer’s site. Once on site, the equipment can be readily assembled and tested saving many hours of on-site labour. This design will also allow the interchangeability of modules depending on the specific customer’s needs.

Utility Demands

A major part of the operating cost is the consumption of utilities and the largest portion of this utility cost is for hydrogen. To ensure complete and clean chemical reactions in the GPCR, the process operates so that there is greater than 50% hydrogen on a molar basis at the reactor outlet. In previous plants this excess hydrogen was then burned as a component of the product gas to provide process heating. In some cases when not enough process heating was required, the excess product gas was simply flared. Recent design improvements include a system to recover this excess hydrogen so that it can be reused.

Table 1 below shows the hydrogen separation and recovery that is expected by using a membrane separation technology that was developed by Air Products. The feed stream is the typical composition of product gas produced when treating high strength organic wastes such as pesticides. The product gas is the gas after the scrubbing step where the HCl and most of the water is removed. The product gas is then heated to 80°C and compressed to 650kPa prior to the hydrogen separation membrane. One can see from Table 1 that the permeate has a high concentration of hydrogen with most of the methane removed. This gas can be recycled and reused, and process modelling using ChemCAD has shown that the overall hydrogen consumption of the process can be reduced by approximately two thirds. This is a significant cost saving. An additional benefit is that the non-permeate volume is greatly reduced and the fuel value properties more closely resemble that of typical gaseous fuels. This will eliminate the need for special burner trains. As well, the reduced volume means that the requirement to flare excess product gas is also reduced.

Staffing

A significant cost associated with operation of the GPCR technology in the past has been the staffing requirements.

<table>
<thead>
<tr>
<th>Stream Name</th>
<th>FEED</th>
<th>NON-PERM</th>
<th>PERMEATE</th>
<th>Summary of Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp (mole %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td>70.00</td>
<td>38.06</td>
<td>89.80</td>
<td>H2 Recovery = 79.20%</td>
</tr>
<tr>
<td>CH4</td>
<td>14.14</td>
<td>33.33</td>
<td>2.24</td>
<td>CH4 Rejection = 90.21%</td>
</tr>
<tr>
<td>CO</td>
<td>9.43</td>
<td>21.31</td>
<td>2.07</td>
<td>CO Rejection = 86.47%</td>
</tr>
<tr>
<td>CO2</td>
<td>4.71</td>
<td>6.37</td>
<td>3.68</td>
<td>CO2 Rejection = 51.76%</td>
</tr>
<tr>
<td>H2O</td>
<td>1.52</td>
<td>0.47</td>
<td>2.17</td>
<td>H2O Rejection = 11.77%</td>
</tr>
<tr>
<td>Bz</td>
<td>0.20</td>
<td>0.46</td>
<td>385 PPM</td>
<td>Bz Rejection = 88.13%</td>
</tr>
<tr>
<td>Flow (Nm3/min)</td>
<td>4.500</td>
<td>1.722</td>
<td>2.778</td>
<td></td>
</tr>
<tr>
<td>Temperature (C)</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Pressure (kPa)</td>
<td>650</td>
<td>580</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Avg MW</td>
<td>8.8239</td>
<td>15.3313</td>
<td>4.7900</td>
<td></td>
</tr>
</tbody>
</table>
Improved equipment reliability, the elimination of black tarry material, and increased automation have all contributed to reducing the number of staff required while maintaining safe and efficient operations.

**Operating Costs**

The total cost of operation varies greatly by the waste type and quantity but it is important to try to address the issue in this paper. As a general rule, the utility requirements are directly proportional to the organic waste throughput. When treating a waste that is only 5% organic for example, the throughput is much higher and the utility consumption only relates to the 5% organic content. The labour requirement however is related to the total throughput capacity of the plant. Larger plants with higher throughput will reduce the labour cost per tonne of waste processed. Utility and labour costs will vary depending upon the location of a given project.

Using the utility and labour rates developed for the UNIDO project in Slovakia, it is estimated that a GPCR plant processing pure pesticide type wastes would have a utility cost of US$1,800 and a labour cost of US$375 per tonne of waste processed.

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**TECHNOLOGY VENDOR UPDATE**

Dr. Douglas Hallett invented the GPCR process, and with Kelvin Campbell, obtained various patents in Canada, the United States, Europe and other jurisdictions world-wide. These patents were assigned to Eco Logic for its exclusive commercial use. In 1998, Dr. Hallett stepped aside as CEO of Eco Logic and he and Mr. Campbell began to develop other new technologies. These included a UV treatment system for drinking water and blood products, and a major internet communications system. In 1999, Dr. Hallett formed an environmental consulting company called Hallett Environmental and Technology Group Inc. Hallett Environmental is a small company that is well known in Canada for directing large environmental clean-ups.

In 2004, Eco Logic ceased operations and Mr. McEwen went to work for Hallett Environmental. The GPCR process remains an excellent technology that it is well suited to the destruction of PCBs, CFCs, pesticides, and other hazardous organic wastes. Hallett, McEwen and Campbell are the original inventors and developers of the GPCR technology and they intend to promote its continued use and development.

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**ЭКОЛОГИЧЕСКИЙ ЭФФЕКТИВНОЕ УПРАВЛЕНИЕ ПЕСТИЦИДАМИ**

Э. МАММАДОВ, И. БАБАЕВ

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**АБСТРАКТ**

In spite of the fact that the chemical industry is working with high perfection, today there are no doubts, that chemical environmental contamination represents the big problem for humanity. Some of the problems became obvious only recently. Pursuing those or other purposes, there have been created many chemicals and numerous groups are represented with pesticides and bring the certain contribution to environmental contamination. On the one hand, pesticides are necessary means of struggle for preservation of foodstuffs. There is sufficient proof to assert, that losses from weeds, wreckers and illnesses without application of pesticides can reach 60% of an annual crop.

On the other hand, use of pesticides in the agriculture is a source of dangerous substances getting in the environment. It is very important to note, that in an environment all pesticides made by the world industry act, anyhow. All of them are toxic and alien substances for life (proof organic products). Besides, there is a stability of wreckers to the whole groups of pesticides. Many pesticides before decomposition in the ground get in water that is used by countrymen for drinking purposes. The contents of proof pesticides in natural waters makes $10^{-2} - 10^{-7}$%. In addition, such small concentration represents serious danger. Harmful influences of pesticides are very great. Especially it is necessary to specify on chlororganic pesticides and dangers connected with dioxins formation. The pesticides produced as a result of chlororganic synthesis even if in the smallest quantities, anyhow, comprise dioxins.

Researches have shown that even initial chlororganic connections already contain a set of polychlorinated dioxins. Having fantastic toxicity, they are widely distributed worldwide.

Work is defined by an ecological orientation and has two interconnected purposes: reduction of application of pesticides in agriculture and non-polluting neutralization of pesticides.

The installation developed to catch superfluous pesticides allows reducing the application of pesticides and the environmental contamination.

Also the electrocatalytical method of cleaning is connected with destruction of aromatic structures that in many respects predetermined with their toxicity. Search for conditions providing complete destruction of aromatic structures is representing one of actual problems.

**АННОТАЦИЯ**

Несмотря на то, что химическая промышленность доведена до высокого совершенства, на сегодня нет никаких сомнений, что химическое загрязнение окружающей среды представляет большую проблему для
всего человечества. Причем некоторые из них стали очевидными только в последнее время. Преследуя те или иные цели, было создано много химикатов, многочисленную группу которых представляют пестициды и вносят определенный вклад в загрязнение окружающей среды. С одной стороны, пестициды являются необходимым средством борьбы за сохранение продуктов питания. Имеются все основания утверждать, что потери от сорняков, вредителей и болезней без применения пестицидов могут достичь 60 % ежегодного урожая.

С другой стороны, использование пестицидов в сельском хозяйстве является источником опасных веществ попадающих в окружающую среду. Очень важно отметить, что в окружающую среду поступают, так или иначе, все пестициды производимые мировой промышленностью. Все они являются токсичными и чуждыми для жизни веществами (стойкими органическими соединениями). Кроме того, появляется устойчивость вредителей к целым группам пестицидов. Многие пестициды до разложения в почве попадают в воду, которая используется сельскими жителями для питья. Содержание стойких пестицидов в природных водах составляет 10–9 — 10–7 %. Но и такие малые концентрации представляют серьезную опасность. Вредные влияния пестицидов очень велики. Особенно следует указать на хлорорганические пестициды и опасности связанные с образованием дioxinов. Пестициды, полученные в результате хлорорганического синтеза, даже в крайне малых количествах, так или иначе, содержат в себе дioxины.

Исследования показали, что даже исходные хлорорганические соединения уже содержат набор полихлорированных дioxинов. Обладая фантастической токсичностью, в последнее время они широко распространяются по всему миру.

Работа определяется экологической направленностью и имеет две взаимосвязанные цели: уменьшение применения пестицидов в сельском хозяйстве и экологически чистую нейтрализацию пестицидов.

Разработанная установка по улавливанию избыточных пестицидов позволяет уменьшить применение пестицидов и загрязнение окружающей среды.

Заслуживает внимания также электрокатализический метод очистки связанный с деструкцией ароматических структур, которые во многом предопределяют их токсичность. Поиск условий обеспечивающих глубокую деструкцию ароматических структур представляет собой одну из актуальных задач.

Проведенные исследования однозначно свидетельствуют, что применение пестицидов при обработке семян приводит к серьезным экологическим последствиям. Предлагаемая технология обработки семян позволяет консервировать избытки пестицидов, тем самым уменьшить загрязнение окружающей среды. Основным элементом данной технологии является осаждение остаточных пестицидов в специальных банках. Возможности данной технологии позволяют осуществлять технологический процесс без повреждения семян и применение пестицидов с минимальным загрязнением окружающей среды. При пуске электродвигателя семена поступают из бункера на транспортер, при встрече с параллелоновой лентой семена, врачаются вокруг оси, протравливаются пестицидами, которыми наполнены банки. Технологический процесс осуществляется с помощью данной установки. Рисунок 1.

Одним из перспективных направлений электрокатализа для решения прикладных задач является химическая экология. Используемые при этом электрокатализические системы многоварианты, что способствует решению широкого круга вопросов, связанных, прежде всего с очисткой воды.

Загрязнение воды пестицидами является одним из основных элементов водной токсикологии. Вследствие растущего потребления фенола и его производных возникла опасность загрязнения фенольсодержащими соединениями. Опасность загрязнения обусловлена устойчивостью к разложению фенола и его производных. Эффективной и окончательной очистки можно достичь с помощью деструктивных методов.

Наиболее эффективным методом очистки сточных вод от этих опасных загрязнителей представляется электрокатализические методы.

Электрокатализические системы многоварианты. Могут сочетать в себе несколько блоков и часто имеют большую разрешающую способность.

При рассмотрении различных вариантов электрокатализических систем, выбор приемлемого варианта базируется на учете целого ряда факторов и, прежде всего на сравнительной оценке каждого из вариантов в отдельности.

Как показывают исследования, проведенные по очистке модельных фенольсодержащих растворов, электрокатализические воздействия резко снизают содержание ароматических структур. В связи с тем, что реальные воды содержат значительное количество хлоридов, представляло интерес изучение их влияния на электрокатализическую очистку растворов. В результате экспериментов было установлено усиление эффектов очистки в присутствии хлоридов, при использовании в качестве анодных материалов, как чистых графитов, так и платинированной платины. Наблюдаемые эффекты обусловлены влиянием,
так называемого «активного хлора», электрохимическая генерация которого несомненно имеет место, когда в электрокаталитической системе присутствуют хлориды. При рассмотрении вопроса о положительном влиянии электрохимической генерации активного хлора на очистку воды от токсичных загрязнителей ароматического характера нельзя обойти молча-нием опасности связанные с возможным возникновением диоксинов. Учитывая исключительно большую токсичность диоксинов, их появление в системе мо-жет с избытком перекрыть положительные эффекты, достигнутые в процессе очистки от исходного загряз-нителя.

Согласно полученных нами экспериментальных данных базирующихся на комплексе современных ана-литических методов, во всех случаях электрохимической генерации активного хлора могут быть достигнуты условия, позволяющие полностью разрушить аромати-ческие ядра фенолов и другие ароматические сое-динения. Кроме того, непосредственные анализы на диоксини, после завершения окисительного воздей-ствия, хотя и носит эпизодический характер, тем не менее, не подтвердили их присутствия.

Заслуживает внимания данные приведенные в таб-лице 1.

Таблица 1. Электрокаталитическая очистка фенолсодержащих вод 

<table>
<thead>
<tr>
<th>Время окисления, мин</th>
<th>Компоненты сточной воды</th>
<th>Процент очистки</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Фенол I</td>
<td>Другие</td>
</tr>
<tr>
<td>0</td>
<td>180</td>
<td>115</td>
</tr>
<tr>
<td>90</td>
<td>8</td>
<td>32</td>
</tr>
<tr>
<td>180</td>
<td>1,2</td>
<td>14</td>
</tr>
</tbody>
</table>

Данные по анализу продуктов анодного окисления фенола в условиях электрохимической генерации ак-тивного хлора указывают не только на то, что все хло-рированные ионы в процессе окисления разрушают-ся, но и свидетельствуют о полной деструкции аро-матических структур с образованием в качестве ко-нечных продуктов углеводородного газа, воды и следов количеств хлороформа.

Объем сточных вод, их состав и технология очистки предопределяют достаточно большое разнообразие ре-акторов электрокаталитических систем. На рисунке 2 приведена схема реактора, работающего в условиях электрохимической генерации активного хлора.

Как видно из схемы, реактор в цеплом включает 3 блока: собственно электрохимический блок (I), ката-литический блок (II) и регенерационный блок (III).

В электрохимическом блоке анодное и катодное пространства изолированы друг от друга пористой мембраной, обеспечивающей требуемую электропро-водность. В данном блоке реализуются две конкури-

![Рисунок 2. Схема реактора, работающего в условиях генерации активного хлора](image)

рующие электрохимические реакции, связанные с электролизом ионов хлора и воды. Разряд ионов хло-ра на аноде, генерирует «активный хлор», распад ко-торого сопровождается образованием высокореакции-оноспособного кислорода, ответственного за очис-тку находящейся в реакторе сточной воды. Образую-щийся при этом молекулярный хлор, а также кисло-род, выделяющийся при разряде молекул воды, нап-равляются в регенерационный блок, где за счет реак-ции гидролиза, молекулярный хлор диспропорциони-рует в хлороводородную и хлорноватистую кислоту, осуществляя тем самым регенерацию хлоридов.

В зависимости от требований, предъявляемых к сте-пени очистки, вода из электрохимического блока мо-жет либо сливаться, либо направляться на доочистку в каталитическом блок, наличие в котором соответст-вующих катализаторов обеспечивает каталитический распад пероксида водорода, а соответственно, и доо-чистку.

В работе было показано, что такие реакторы опра-вывают себя, при очистке сточных вод, обогащенных хлоридами и содержащими компоненты ароматичес-кого характера (фенолы, ПАВ и др.).

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