BIOCATALYTIC DECHLORINATION OF LINDANE BY NANOPARTICLES OF PD(0) DEPOSITED ON SHEWANELLA ONEIDENSIS

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ABSTRACT

This study concerns a new approach for the removal of the pesticide lindane. Although several HCH degradation techniques exist, they often suffer from disadvantages as e.g. conversion to more toxic compounds, slow degradation rate, or stereoselectivity towards some isomers only. A possible degradation method for HCH is the catalytic reduction to benzene over metal catalysts, e.g. Pd(0). Since specific surface area plays an important role in reactivity of catalysts, this study investigated the use of bioPd(0), i.e. nanoscaled Pd(0) particles precipitated on the biomass of Shewanella oneidensis, for the removal of lindane. It was demonstrated that bioPd(0) has catalytic activity towards dechlorination of $\gamma-$HCH, with formate as electron donor, and that dechlorination with bioPd(0) was more efficient than with commercially available powdered Pd(0). Furthermore, catalytic dechlorination was shown for other HCH isomers. The results of this work showed that an efficient and fast removal of lindane was achieved by biocatalysis with bioPd(0). Moreover, the easily biodegradable benzene is formed as reaction product and stereoselectivity of isomers does not occur. This dechlorination technique may therefore contribute to the search for better alternatives to the current remediation technologies of HCHs.

Key words: $\gamma-$hexachlorocyclohexane, HCH, bioPd(0), Shewanella oneidensis, palladization, reductive dechlorination, bioremediation, biocatalysis

INTRODUCTION

Lindane ($\gamma-$hexachlorocyclohexane, $\gamma-$HCH) is an organochlorine insecticide that has been produced and used worldwide [1]. The production process of $\gamma-$HCH yields about 85% of non-insecticidal HCH isomers (mainly $\alpha-$, â- and ä-HCH). Although most countries have prohibited the production and use of $\gamma-$HCH, some countries are still using the pesticide. Due to their widespread use and because of their relative high resistance to degradation, $\gamma-$HCH and other HCH isomers have been observed frequently in soils and groundwaters all over the world [2], causing a major environmental problem.

Several methods for the elimination of lindane and its wastes exist. Although combustion is the cheapest method, it is undesirable because of the formation of even more toxic polychlorinated dioxins [3]. Despite its persistence, HCH biodegradation has been reported in various aerobic and anaerobic environments [4, 5]. There are numerous reports of HCH-degrading microorganisms. Unfortunately, microbial degradation of HCH isomers proceeds rather slowly, and most bacteria cannot degrade all HCH-isomers [6, 7]. Another possible degradation method for HCH is the catalytic reduction over metal catalysts. The advantages that these catalytic processes offer are both environmental and commercial (milder conditions, elimination of toxic and expensive reagents, ease of catalyst/ product separation, good selectivity and yields). The use of Pd as catalyst for the elimination of lindane has been reported [8, 9]. The reaction was shown to give benzene under atmospheric pressure.

Specific surface area plays an important role in catalytic reduction reactions, since a larger specific surface increases the reactivity of the catalyst. Shewanella oneidensis, a versatile metal reducing species [10], is known for its ability to precipitate metal nano-particles which are either formed de novo by bioreduction or adsorbed from the surrounding medium [11-13]. More specifically, De Windt et al. [14] described the bioreductive deposition of palladium (0) nanoparticles on Shewanella oneidensis. This so-called bioPd(0) has the ability to reductively dehalogenate PCBs. Because of the large specific surface area, dechlorination of PCBs with bioPd(0) was found to be more efficient than with commercially available powdered Pd(0).

The objective of this study was to demonstrate catalytic activity of bioPd(0) towards dechlorination of $\gamma-$HCH. In addition, the non-specificity of the dechlorination was assessed by evaluating the catalytic activity of bioPd(0) for HCH isomers other than the ã isomer.

MATERIALS AND METHODS

Bacterial strains and growth conditions

Shewanella oneidensis MR-1 was obtained from the BCCM/LMG Bacterium Collection (Ghent, Belgium) under the number LMG 19005. The strains were grown aerobically in Luria-Bertani (LB) medium [15] (overnight at 28 °C).

Bioreduction of Pd(II) to bioPd(0) by Shewanella oneidensis

Formation of bioPd(0) was done as described by De Windt et al. [14]. In short, S. oneidensis MR-1 cells were harvested from an overnight LB culture in sterile 50 ml centrifuge tubes (TTP, Switzerland) by centrifuging at 3000 g for 10 min. Afterwards the cells were resuspended in 30 ml M9 medium [15] in glass serum bottles. Serum bottles were capped with inert viton stoppers. Control bottles containing no cells were included in the set-up. The cell suspension was supplemented with 1.1 mg formate l^{-1} formate (as sodium formate) as organic electron donor. Finally, 50 mg Pd(II) l^{-1} was added as Na_2PdCl_4 (Sigma-Aldrich, Seelze, Germany). The serum bottles were then incubated overnight at 28 °C. All assays were set up in triplicate.

Dechlorination of g-HCH by bioPd(0): Proof of principle

In a first experimental set-up, bioPd(0), i.e. a suspension of palladized cells obtained from the bioreduction of Pd(II) by S. oneidensis MR-1 as described above, was supplemented with sodium 1.1 mg formate l^{-1} as e-donor to activate the Pd catalytic particles. Controls consisted of i) M9 medium supplemented with commercial Pd(0) powder (Sigma-Aldrich, Seelze, Germany) at the same concentration as the bioPd(0) and ii) S. oneidensis MR-1 cells suspended in M9 medium supplemented with formate but without Pd(II) or Pd(0). $\gamma-$HCH was added to each set-up at a concentration of 50 mg l^{-1} from a DMSO stock solution, after which the bottles were incubated (28 °C, 115 rpm). All assays were set up in triplicate. Samples were taken for $\gamma-$HCH analysis by SPE followed by GC-ECD.

Non-specificity of bioPd(0) catalytic dechlorination of HCH

Non-specificity of the HCH dechlorination was investigated by subjecting other HCH isomers than $\gamma-$HCH, i.e. α-, β- and γ-HCH, to the catalytic reaction with bioPd(0). BioPd(0) was again obtained as described above. Three set-ups of bioPd(0) suspension were prepared similar to the first experimental set-up, i.e. the bioPd(0) suspensions were supplemented with sodium 1.1 mg formate l^{-1} and α-, β- and γ-HCH were added to these three different set-ups at a concentration of 50 mg l^{-1} from a DMSO stock solution, after which the bottles were incubated (28 °C, 115 rpm). All assays were set up in triplicate. Samples were taken for HCH analysis by SPE followed by GC-ECD.

ANALYTICAL METHODS

Analysis of HCH isomers from watery suspensions was performed by first extracting HCH from a 2 mL sample using C18 SPE columns (product code 12102025, Bond Elut®, Varian, Harbor City, CA, USA) according to the manufacturer's instructions. Subsequently samples were analyzed by GC (CP-3800, Varian) with an electron capture detector. GC conditions were: injection temperature = 225 °C; detector temperature = 300 °C; initial column temperature = 100 °C (hold 2 min), increase to 160 °C at a rate of 15 °C/min, increase to 270 °C at a rate of 5 °C/min; column pressure = 16 psi. The column used was a Factor FourTM low bleed capillary column (VF-5ms, 30m x 0,25 mm ID DF=0,25, Varian) (Method 8081A, EPA). Technological Centre GAIKER (Zamudio, Spain) performed GC-MS analysis for the detection of dechlorination products in the liquid fraction and headspace.

RESULTS AND DISCUSSION

Dechlorination of $\gamma-$HCH by bioPd(0): Proof of principle

In a first stage of the research, the goal was to prove the

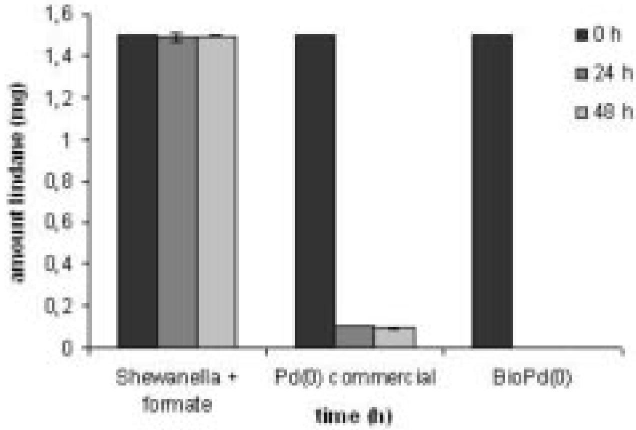

Figure 1. Lindane removal presented as remaining amount of lindane (mg) in different treatments. "Shewanella + formate" represents a control set-up with non-palladized cells, "Pd(0) commercial" shows catalytic lindane removal by commercial Pd(0) powder and "BioPd(0)" shows biocatalytic lindane removal by bioPd(0)

principle of dechlorination of lindane ($\gamma-$HCH) by bioPd(0) with formate as electron donor. The performance of dechlorination by bioPd(0) was compared to dechlorination by commercial Pd(0) powder. As can be seen from Figure 1, both commercial Pd(0) and bioPd(0) were able to remove lindane after 24 h. However, the removal by bioPd(0) was significantly higher ($P<0.001$). The control consisting of non-palladized S. oneidensis MR-1 cells supplied with formate, did not show any removal of $\gamma-$HCH. GC-MS was used to detect possible dechlorination products or intermediates of the dechlorination of $\gamma-$HCH by bioPd(0). No potential dechlorination products were found in the liquid phase (data not shown). GC-MS analysis of the gas phase, however, showed a significant peak representing benzene.

The use of Pd(0) as catalyst for the conversion of lindane to benzene has been reported earlier [8, 9]. However, here it is shown that $\gamma-$HCH removal with bioPd(0) and formate as electron donor was significantly higher than with commercial Pd(0). An increased reactivity of nano-scale catalytic particles towards recalcitrant halogenated compounds was hypothesized earlier by Baxter-Plant et al. [16] and the efficiency of bioPd(0) for the dehalogenation of PCBs has been shown earlier by De Windt et al. [14].

Non-specificity of bioPd(0) catalytic dechlorination of HCH

Figure 2 shows the biocatalytic dechlorination of other HCH isomers than γ-HCH, namely α-, β- and δ-HCH. All three HCH isomers were readily dechlorinated after a few hours, although a concentration of 1.5 to 3 mg l^{-1} remained over a period of about 45 h. However, after measurement of the residual concentration of the different HCH isomers after 25 days, it was found that a nearly complete HCH removal was established for all isomers (Table 1).

In conclusion, compared to other degradation techniques for HCH, which may suf-

Table 1 Residues (expressed as the percentage of the initial HCH concentration) of α-, β- and δ-HCH

	HCH residue (% of initial conc)
α-HCH	0.5 + 0.1 γ-HCH (isomerisation)
β-HCH	0.1
δ-HCH	0.0

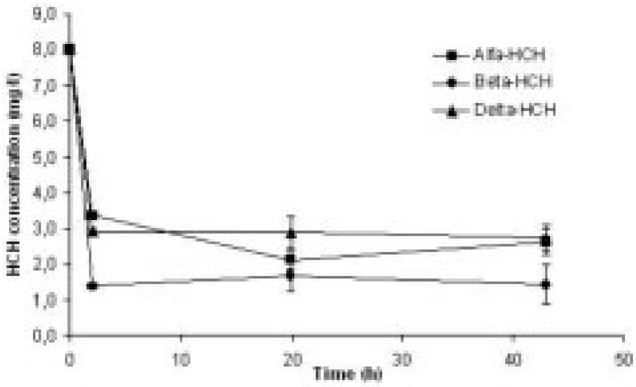

Figure 2. Biocatalytic dechlorination of α-, β- and δ-HCH with bioPd(0)

fer from many disadvantages, as e.g. the conversion to more toxic compounds, slow degradation rate, or stereoselectivity towards some isomers only, this technology converts HCH into the easily biodegradable benzene. Moreover, stereoselectivity towards some isomers does not occur. Therefore, this technique may contribute to the search for better alternatives for the current remediation technologies of HCHs.

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A SYNTHESIS AND A CRITICAL REVIEW ON THE TREATMENT OF POLLUTED SITES WITH HCH-ISOMERS

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ABSTRACT

Since 1940, technical HCH and lindane have been widely used as insecticides. But their persistence in the environment and their harmfulness to health motivated their ban in some countries since 1970. The progressive ban of HCH results in obsolete HCH stockpiles.

In most cases, facing the risk to human health and the environment, the first priority is to confine the site with an upper clay wall to avoid the pollution leaching. Then, according to the treatment feasibility, as well as the economics of the situation, a remediation policy is chosen.

This paper presents a critical review of real cases of HCH contaminated soil and groundwater remediation.

Keywords: HCH, soil remediation, groundwater remediation, thermal desorption, chemical extraction, bioremediation, base catalysed degradation, funnel and gate, pump-and-treat treatment.

INTRODUCTION

Since 1940, technical HCH and lindane have widely been used as insecticides. But their persistence in the environment and their harmfulness to the health motivated their ban in some countries in 1970. The progressive ban of HCH results in obsolete HCH stockpiles. They are often discharged without any care at a landfill. As a result, some highly polluted sites exist with a risk of a contamination of the nearby soil and the underground water. In France, among the 46 listed sites concerning a pesticide soil or/and groundwater contamination, 12 are subject to lindane or HCH residues.

In most cases, facing the risk to human health and the environment, the first emergency is to confine the site with a clay upper wall to avoid the pollution leaching. Then, according to the treatment feasibility and the economy, a remediation policy is chosen.

This paper deals with a critical review of real cases of HCH contaminated soil and groundwater remediation. Soil and stockpiles still applied are thermal desorption, liquid extraction, bioremediation and base catalysed decomposition.

The remediation of groundwater polluted by HCH, discussed in this review, relies on the reactive barriers filled with activated in situ bioremediation and pump-and-treat system.

SOIL TREATMENT

Remediation techniques are usually separated in two categories: thermal methods (incineration, thermal desorption) are separated from others. Nevertheless, if incineration reduces the contaminated soil into ashes, it leads to the formation of dioxins or furans, which are toxic combustion by-products. Alternative solutions to incineration are encouraged.

Treatment experiences of HCH contaminated soils by thermal desorption, chemical extraction, bioremediation and base catalyse decontamination have been reported:

THERMAL DESORPTION

During thermal desorption, the contaminated soil is heated at 400 – 600 °C. The contaminant is vaporised and transferred in the gas phase before being destroyed in a post-combustion of the gas (Silcox et al., 1995). The soil matrix can be recycled in civil engineering.

In their desorption unit in Rotterdam, Ecotechniek reduced the contamination of 1,200 tonnes of soil (2300 $mg.kg^{-1}$ Dry Matter a-HCH, 550 $mg.kg^{-1}$ DM b-HCH, less than 1 $mg.kg^{-1}$ DM g- HCH and 15 $mg.kg^{-1}$ DM d-HCH) to less than 0.1 $mg.kg^{-1}$ of each isomer. Another 60,000 tonnes soil contaminated by 1500 $mg.kg^{-1}$ of lindane were treated in Rotterdam before reuse in public works (Agassi et al., 1998).

GRANULOMETRIC SEPARATION AND CHEMICAL EXTRACTION

The extraction transfers the contaminant into a liquid phase (Methanol, isopropanol, acetone) allowing easier further treatment (Salas et al., 1998). Three successive extractions with a yield of 90.99 and 50 % reduce the HCH contamination from 2464 to 0.25 $mg.kg^{-1}$, in isopropanol as well as in acetone. The chemical extraction can be done on a specific granulometric slide, which is the more polluted (Cuyten, 1998). In the 90's, Heijmans Milieutechniek has treated 220,000 t of soil contaminated by 18 $mg.kg^{-1}$ HCH and 15 $mg.kg^{-1}$ Hg in their physico-chemical treatment unit in Rosmalen (NL) at a rate of 10 to 18 $t.h^{-1}$. This process first separates the clay and the organic matter before extracting the pollutants. This process leads to 20 – 30% highly contaminated sludge and 70-80% sand, reusable in public works. As a result, the soil was decontaminated more than 99.8% (Cuyten, 1998).

A sandy, silty soil contaminated by 2,300 $mg.kg^{-1}$ a-HCH has been treated in the SOLVIS treatment unit of ATE - GEOCLEAN SA (France) using methylene chloride as a solvent at 6 $t.h^{-1}$. The residual concentration was 12 $mg.kg^{-1}$ (Modolo and Villemagne, 1998).

BIOREMEDIATION

A complete bioremediation leads to the pollutant mineralisation by stimulating the micro-organism activity. In the case of HCH, anaerobic conditions are needed since b-HCH is recalcitrant to aerobic degradation. First the contaminated soil is amended with organic matter as a nutrient for stimulating the indigenous micro-organism activity. Moreover, these amendments offer non toxic site for micro-organism to develop. A water supply favours the contact between micro-organisms and pollutants. In a second step anaerobic conditions are generated with (Phillips et al., 2001):

- Metal (ex: Fe) to favour the dioxygen scavenging (DARAMEND® process)
- Water for preserving anaerobic conditions and favour the micro-organism / contaminant contact.

Under anaerobic conditions, reductive dechlorination occurs: HCH degradation results in the replacement of chloride atoms by hydrogen leading to benzene, monochlorobenzene and chlorophenol. These compounds are in a second aerobic step degraded into CO_2 and CH_4. Aerobic conditions are obtained after soil drying or soil mixing.

The DARAMEND® process has been applied on a former lindane production site in Kentucky (USA). After 15 anaerobic – aerobic cycles (251 days), the 95 $mg.kg^{-1}$ of lindane have been reduced to 5 $mg.kg^{-1}$. As a global result, the decontamination level of the 4,122 $g.kg^{-1}$ HCH mixture was at 92% (Langenhoff et al., 2001).

BASE CATALYSED DEGRADATION

Base catalysed degradation has been developed in the 1990s, especially for halogenated compounds. Liquid and solid wastes are treated in the presence of a boiling-point hydrocarbon, sodium hydroxide and a proprietary catalyst. Near 300°C, highly reactive atomic hydrogen is produced and cleaves the C-Cl bonds. Decomposition products are carbon and sodium chloride. They are separated from the unreacted oil by gravity or centrifugation.

For contaminated soils, contaminants are first extracted in a thermal desorption step and condensed.

BCD has largely been applied on soil contaminated by PCB, dioxins and furans. On a former lindane manufacture located in Bilbao (Spain), 3500 t of HCH residue have been treated using BCD. In this case of study, HCH has not been destructed but converted into trichlorobenzene (Barquin, 1998, Barquin 2001).

DISCUSSION

Lots of techniques provide a good remediation basis for soil contaminated with HCH isomers. The choice will depend on the pollution spread, depth, concentration and environmental and human risks nearby the site. Often, the remediation costs play a major role in the final decision.

Bioremediation, in-situ or after excavation, is a tempting technique, as it is very smooth. But it takes several years before a medium remediation is achieved and the remediation control is difficult because of its inhomogeneity. Chemical extraction is efficient but needs the treatment of extraction solutions which often leads to incineration.

Thermal desorption has shown good results but the desorbed gases are destroyed in a post-combustion chamber with the risk of formation of dioxins and furans. The gas phase chemical reduction of pollutants would offer a good alternative to post combustion. Introduction of dihydrogen promotes a reductive atmosphere that avoids the formation of dioxins and furans. Some successful experiences exist about soils contaminated with PCB but not again about HCH. It should be well adapted to HCH decontamination.

Finally it must be noticed that once decontaminated, the soil can be used for civil works or, if not enough decontaminated, it has to be put in discharge.

GROUNDWATER REMEDIATION

Three ways for the groundwater treatment exist. The polluted groundwater is pumped and treated in an upper treatment station (pump-and-treat technology), a reactive material is injected in-situ or a permeable reactive barrier is placed vertically to the flow path allowing its treatment. When the contaminated plume is large, a funnel and gate barrier is installed. It consists of a permeable gate placed between two impermeable walls that redirect the plume towards the reactive barrier. The permeable barrier contains a material that immobilises or decomposes the contaminant (Xenedis et al., 2000).

PUMP AND TREAT SYSTEM OF HCH CONTAMINATED GROUNDWATER

Among the water treatment adapted to HCH removal, water filtration should be adapted. But it needs a pre-treatment stage for preserving the membrane from fouling. Chemical oxidation of HCH seems to be not efficient enough (Ollis et al., 1991) although photochemical oxidation has shown encouraging laboratory results (Dionysiou et al., 2000).

Bioreactors or activated carbon adsorption have already been used to remove HCH in a pump-and-treat system. Kouras et al. (1998) have shown that 20 $mg.L^{-1}$ powder activated carbon were necessary to reduce 10 $\mu g.L^{-1}$ of lindane to 1 $\mu g.L^{-1}$ in one hour. Activated carbon is efficient at low concentration (less than a few $mg.L^{-1}$). Suspended matter (> 50 $mg.L^{-1}$) or greasee (>10 $mg.L^{-1}$) favour the activated carbon fouling (Kouras et al., 1998).

Powdered activated carbon has been used in the pump-and-treat system for the Ott/Story/Cordova (USA) groundwater contaminated with a cocktail of pesticides and halogenated COV and for the Baird and Mc Guire (USA) site polluted by PAH and pesticides.

Groundwater contaminated by lindane and DDT produced by Ciba Geigy at McIntosh (Alabama, USA) are treated for several years in a bioreactor before being let out in a nearby river.

IN-SITU REMEDIATION

As expected from the pump-and-treat system efficiency, the best adapted material to fill a reactive barrier is activated carbon.

The remediation of the groundwater from Marzone Inc., Chevron Chemical Company at Tifton (USA) contaminated with a -HCH (60 $mg.L^{-1}$), b-HCH (98,5 $mg.L^{-1}$) and lindane (54,6 $mg.L^{-1}$) has been achieved with a funnel and gate barrier filled with 780 kg activated carbon. The residual concentrations of a-HCH, b-HCH and g-HCH below the gate are 0,03, 0,1 et 0,77 $\mu g.L^{-1}$ respectively.

A biological in-situ remediation has been completed by TNO in the Netherlands between 2001 and 2003 on a former lindane production site. Remediation was achieved in two steps, the first one consisting of the creation of an anaerobic zone in the groundwater. This first step was essential since anaerobic conditions favour the HCH biodegradation, especially the b-HCH which is recalcitrant to aerobic degradation. This in-situ biodegradation led to the HCH transformation into benzene and monochlorobenzene, which were further degraded in a second step, consisting of an aerobic digestion in a reactor after pumping the groundwater. Following this two-step biological treatment, HCH was successfully removed, as no more was detected.

DISCUSSION

The pump-and-treat technology offers a larger choice of treatment technologies than in situ decontamination: filtration, bioreactor, photochemical decontamination, adsorption on activated carbon.

For in situ decontamination of HCH polluted groundwater, there are fewer choices. Injection of bacteria, adsorption of activated carbon seems well adapted,). Bioremediation has shown good results in the TNO experience, as well as less good ones (Frasar, 2000).

The most adapted technique seems to be adsorption on activated carbon and whatever the operation system (gate, pump and treat methodology): a successful experience exists at the Marzone site.

CONCLUSION

Before any treatment, the pollution source (stockpile, polluted soil) has to be contained for limiting the pollution dispersion and the groundwater or nearby river contamination. After that, a remediation technique for contaminated soil has to be selected according to the pollution spread, accessibility and concentration. For soil remediation, lots of solutions exist: a comprise has to be made between the remediation efficiency and by-product pollution such as dioxins and furans in combustion processes.

If a treatment for groundwater is required as well, pollution has to be confined and then groundwater must either be redirected through a funnel and gate or pumped for treatment. But whatever the methodology, the groundwater decontamination is limited by the presence of non-aqueous phase liquids and contaminants adsorbed on organic matter, which liberates the contaminant slowly. Groundwater can also be persistent and operation can take several years.

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UPTAKE AND TRANSLOCATION OF DDT IN NATIVE PLANTS AT A CONTAMINATED SITE IN CANADA

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ABSTRACT

Since the discovery of its insecticidal properties and its subsequent widespread use, DDT has accumulated in the environment, having a wide range of adverse effects on non-target species. Due to its hydrophobicity, DDT and its metabolites (DDD and DDE) are difficult to remove from contaminated soils, especially after years of weathering processes. The present study investigated DDT uptake and partitioning in native plants from a DDT-contaminated site in the Canadian Arctic. Native plant species (Elymus mollis and Salix arctica) were directly harvested from DDT-contaminated soil at Kittigazuit, NWT to determine the extent of their natural ability to take up and translocate DDT. This site is a former Long Range Aid to Navigation site, and was sprayed daily with DDT to control mosquito populations between 1947-50. Soil DDT concentrations at Kittigazuit range from 20 - 205 000 ng/g, with the majority of samples exceeding the Canadian criteria for DDT in soil (i.e. 700 ng/g). Kittigazuit plants were separated into root, shoot, and leaf segments. Soil and plant samples were analyzed at the Analytical Services Unit at Queen's University using US EPA lab methods 8081 for organochlorine pesticides by gas chromatography, and 3640 for gel permeation cleanup. The potential and limitations of phytoremediation are considered using calculations of risk posed to resident herbivores (Spermophilus paryii).

INTRODUCTION

DDT (dichlorodiphenyltrichloroethane) is a chlorinated organic pesticide that is known to be a toxic and persistent pollutant (ASTDR, 1994; EC, 1998). In 1945, DDT pesticides became available to the Canadian public and were used primarily for agricultural purposes (EC, 1998). As early as the 1950s, it was noted that DDT and its related compounds, DDE (dichlorodiphphenyldichloroethylene) and DDD (dichlorodiphenyldichloroethane), were able to bioaccumulate and biomagnify in the environment (Lawless, 1977). Recently, Canada classified DDT as a Track 1 substance under the federal Toxic Substances Management Policy because it is persistent, bioaccumulative, as well as anthropogenic and is therefore targeted for virtual elimination from the environment (EC, 1997).

Terrestrial plants can act as significant pathways for DDT exposure to receptors in the ecosystem. Uptake into plants is the first step towards the bioaccumulation of DDT in the terrestrial food web (Trapp, 1993). Three main pathways for chemical movement from soils to plants exist: i) root uptake into conduction channels and subsequent translocation, ii) uptake from vapour in the surrounding air, and iii) uptake by external contamination of shoots by soil and dust, followed by retention in the cuticle or penetration through it (Bell & Failey, 1991).

Numerous sites across Canada (and the world) are contaminated with chlorinated organic compounds such as DDT. The past decade has seen efforts to search out alternative techniques (to the classical excavate-and-landfill scenario) to remediate such sites. An area of particular interest has been the development of 'green' or plant-based technologies to remediate contaminated sites. Phytoremediation, which involves growing plants to take advantage of their natural ability to accumulate and/or degrade contaminants, has the potential to transform the way we look at cleaning these sites.

Previous studies have examined phytoremediation of DDT in greenhouse settings, and most often using cell cultures or freshly spiked soil. The current study examines phytoremediation of DDT and risk potential at an actual field site. The research presented here was conducted at an abandoned Long Range Aid to Navigation (LORAN) station located on the Mackenzie River delta at Kittigazuit, Northwest Territories. The LORAN station was occupied from June 1948 to March 1950, during which time DDT pesticide was liberally sprayed to control mosquitoes (Hart & Cockney, 1999). An overview of the work is presented here; details are presented in Zeeb et al. (in prep.).

METHODS

1. Plant Collection

Two species of plants were collected: Salix arctica and Elymus mollis. S. arctica is from the family Salicaceae, commonly known as the willow family. It is a low-growing, dioecious shrub with trailing branches and elliptic or broadly-rounded leaves which are pale green in colour when mature (Porsild and Cody, 1980). It is the most abundant of the arctic willow species, with the most northerly distribution, and provides food for insects, voles, lemmings, hares, and larger arctic mammals such as caribou and muskox. It is a perennial, and although it produces flowers and seeds, much of its biomass consists of vegetatively reproduced branches, which live anywhere from 30-100 years, before dying and being replaced (Savile, 1972). Similarily, E. mollis produces much of its biomass vegetatively. It is a perennial grass, has broad, flat leaves, grows 15-100 cm tall, and can be found in dunes and sandy soils close to water (Porsild and Cody, 1980).

Plant samples were collected as whole specimens, inclusive of root and shoot portions. These samples represented the dominant vegetation in the area, as well as potential forage for animals. Where possible, samples of both species were collected from the same location. A soil sample associated with each plant sample was also collected. Plants were removed using hand tools, and temporarily stored in Ziploc® bags. Within 24 hours of collection, plants were washed thoroughly, and rinsed using potable water. Specimens were dried using absorbent towels, wrapped in sterile aluminium foil, and sealed in clean Ziploc® bags. Samples were catalogued, and frozen.

2. Analytical Procedure

The study plants were kept frozen at the Royal Military College in Kingston, Ontario until use. At that time, they were partitioned into various compartments (e.g. root, shoot, leaf, stem). Samples were air dried, weighed, and ground with sodium sulphate to remove excess moisture. Each soil sample was inoculated with 100 ìl of 50 ppm decachlorobiphenyl (DCBP) surrogate, while 100 ìl of 1 ppm DCBP was added to each plant sample, in order to determine extraction efficiencies. Soil samples were compared to a control of 20 g Ottawa sand and 40 g of anhydrous sodium sulphate, spiked with 100 ìl of 10 ppm of Appendix IX pesticide mix (catalogue # 46960-U from Sigma-Aldrich Co.), while plant samples were compared to a control sample spiked with 100 ìl of 50 ppm of the same pesticide mix. For quality assurance/ quality control, all analytical runs of up to nine samples included a control, a duplicate, and a blank. Blanks were prepared with 40 g of anhydrous sodium sulphate and 20 g of Ottawa sand, spiked with 100 ìL of DCBP surrogate. Samples were extracted using 250 mL of dichloromethane (DCM) in the Soxhlet apparatus for 4-6 hours. Once extraction was complete, samples were concentrated to approximately 10 mL by rotoevaporation at 40°C. Solvent exchange was then performed, by adding approximately 10 mL of hexane to the sample and performing another rotoevaporation. This was repeated twice more in order to replace the DCM solvent in the samples with hexane to allow for accurate gas chromatography / electron capture detection (GC/ECD). The concentrated samples were then rinsed from their round-bottom flasks with hexane, and filtered through florisil columns into 10 ml volumetric flasks, from which they were transferred into GC vials. Samples were loaded onto an agilent 6809 Gas Chromatograph and Electron Capture Detector (GC/ECD) was used to calculate the composition and quantity of ?DDT. A calibration curve was developed using DCBP concentrations of

10, 50, 100 and 200 ppb and a 100 ppb standard was used for each batch of nine samples. All blanks were below sample detection limits and controls were within acceptable limits of the control target as set by EPA method 8250A (EPA, 1994). Surrogate recovery was between 72.1 and 106.3% for the first round of analysis. All were corrected for surrogate recovery, and results were expressed as nanograms of pesticide per gram of dry weight (ng/g). GC/ECD analysis provided metabolite concentrations in ng/g for 2,4-DDE, 4,4-DDE, 2,4-DDD, 4,4-DDD, 2,4-DDT , and 4,4-DDT in each sample. These were summed to provide total DDT concentrations in each plant sample (?DDT).

3. Herbivore Collection & Analysis

Arctic ground squirrels (Spermophilus parryi) were collected using large Victor® rat traps, Havahart® live animal traps, or a .22-calibre rifle. Length, body mass, liver mass, and sex were recorded for each specimen regardless of the collection method. Whole livers were excised using dissection tools, which were cleaned with hexane between specimens. Livers were wrapped in sterile aluminium foil, and sealed in clean Ziploc® bags. Samples were catalogued, and frozen.

In total, 23 S. parryi livers were analysed. Analytical methods were identical to those described above for plant tissue analysis, with a few exceptions. Following extraction and prior to clean-up, the eluent was concentrated and sub-sampled for gravimetric lipid analysis. Results were obtained for all six compounds of SDDT, and were reported as nanograms of pesticide per gram wet weight of animal tissue, and subsequently were lipid-normalized.

4. Risk Assessment

In order to assess risk, an estimation of total daily intake (TDI) of SDDT by S. parryi was calculated using U.S. EPA and CCME exposure equations in Monte Carlo simulation software. In Monte Carlo simulation, a model is analysed in an iterative manner with varying input parameters, where uncertain variables are expressed as distributions rather than fixed values (CCME, 1997). Monte Carlo simulations were performed using @Risk (Version 4) software. The equation for calculation of TDI was as follows (CCME, 1997):

$$TDI = EDI_{soil} + EDI_{plant}$$

where,

$$EDI_{soil} = C_{soil} \times SIR \times F_{soil} \times BA \times AU / BW$$

and,

$$EDI_{plant} = C_{plant} \times PIR \times F_{plant} \times BA \times AU / BW$$

When calculating TDI, several conservative assumptions are made in modelling the soil-plant-herbivore pathway (CCME, 1997):

- 100% of the contaminant exposure of the herbivore originated from the ingestion of contaminated soil and food.
- The herbivore remained on the contaminated site 100% of the time.
- 100% of the food ingested by the herbivore was consumed from the contaminated site.

Accordingly, this study only considered exposure via the ingestion of contaminated soil or plants. Exposure via contaminated drinking water, dermal contact with contaminated soil, and inhalation of contaminant vapour were not considered. Following the calculation of TDI values from S. arctica and E. mollis, dosages were used to estimate expected DDT liver burdens in arctic ground squirrels. Expected liver burdens were also calculated using the soil-leaf-mammal food chain BAF calculated by Jongbloed et al. (1996). Toxic effects were investigated by comparing liver somatic indices (LSI) with SDDT concentrations in livers. Liver enlargement is one of the potential effects resulting from DDT exposure (Smith, 1991; ASTDR, 1994). LSI expresses liver size corrected for the body size for an organism. Liver somatic index (LSI) was calculated according to the equation:

$$LSI = \text{liver weight} / (\text{total weight} - \text{liver weight})$$

RESULTS & DISCUSSION

E. mollis was found to be growing in more contaminated areas of the site than S. arctica. Growing in a maximum SDDT soil concentration of 13200 ng/g, E. mollis accumulated 19600 ng/g SDDT in the roots and 4920 ng/g in the shoots. In this particular study, S. arctica was found growing in a maximum SDDT soil concentration of 3420 ng/g. Under these conditions, it accumulated a 3050 ng/g SDDT in the root, 1680 ng/g in the leaf, and 360 ng/g in the stem tissue. Hence, allowing for differences in soil concentrations, ?DDT concentrations were distributed differently between compartments in the S. arctica and E. mollis plants, with E. mollis sequestering a greater proportion of ?DDT in its roots, and S. artica partitioning its ?DDT more evenly between its root and shoot compartments. The SDDT composition in both plant species demonstrated DDT accumulation, without subsequent metabolism in plant tissue (data not shown). The observed concentrations of SDDT in plants demonstrate the mobility of contaminants from the soil, and shows that plants are a potential route of contaminant exposure for terrestrial animals. Although the spraying of DDT at Kittigazuit ceased over 50 years ago, this study presents evidence that much DDT remains and continues to be taken up by plants.

Ground squirrel (S. parryi) samples from the contaminated site had a maximum SDDT concentration of 4300 ng/g with a median of 140 ng/g. These data for arctic ground squirrels provided a mammalian receptor with which to investigate the impact of DDT contamination. Arctic ground squirrels from areas not impacted by contamination contained much lower (4.5 ng/g) levels of SDDT.

The composition of SDDT compounds in animal tissue indicated the persistent hazard posed by contamination at the site. The known ecology of arctic ground squirrels allowed for the modelling of DDT exposure through the ingestion of contaminated plants and soil. Despite the low estimated dosage (10-150 ng/g), a toxicological effect was observed in arctic ground squirrels. Increases in liver size were significantly correlated with SDDT concentrations (data not shown). The life cycle of arctic ground squirrels might explain the observed effect. During hibernation, arctic ground squirrels rely on stored fat, and during metabolism, potentially toxic amounts of DDT could be released and result in the observed effects.

This study shows that DDT can be preferentially taken up by certain plant species in an actual field setting, and hence there is a real potential for phytoremediation at this site. Phytoremediation has the advantage of being a cost effective, aesthetically pleasing, green technology. It also creates habitat, promotes biodiversity, and prevents further contaminant runoff and/or erosion without creating toxic byproducts. For these reasons, phytoremediation of low to moderate contaminant concentrations offers an opportunity under controlled conditions to clean up soils over a large land area. However, this study also shows that in addition to the usual limitations of depth of root system and requiring a longer time frame than traditional remediation technologies, there are certain precautions that need to be taken when instituting this biotechnology at an actual field site. The potential for transfer up the food chain may result in real risks to resident herbivores. Hence, there is a need for controlled site access (through fencing etc.) to mitigate risk to potential receptors.

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INTRINSIC AND STIMULATED IN SITU BIODEGRADATION OF HEXACHLOROCYCLOHEXANE (HCH)

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ABSTRACT

The contamination of soil and groundwater with hexachlorocyclohexane (HCH) has caused serious environmental problems. Lindane (g-HCH) has been produced as the effective insecticide component of HCH and the remaining isomers a-, ß- and d-HCH were separated from g-HCH and dumped, resulting in contamination. In contrast to a-, g-, and d-HCH, ß-HCH was for a long time known to be recalcitrant towards biodegradation. However, fundamental research has shown that ß-HCH can be degraded to monochlorobenzene and benzene under anaerobic conditions. Complete mineralization of all isomers can thus be reached. The objective of our study was to demonstrate the in situ degradation of HCH at an industrial site.

At the contaminated site a container terminal was constructed at the border of the canal forming the boundary of the site. The surface water of the canal needs to be protected against HCH contamination. Infiltration facilities were installed under this container terminal to create an anaerobic bioscreen. An aerobic zone for the degradation of the formed intermediates monochlorobenzene and benzene follows this anaerobic zone.

The bioscreen is in use since 2001. The concentration of HCH is near detection limit (0.01 µg/l), and the concentrations of monochlorobenzene and benzene are increasing or at a steady state value. HCH has a low availability and is immediately degraded after desorption from the soil particles.

The presentation will include a project overview, field results of four years of the demonstration project and con-

clusive results that the degradation of HCH is the result of the addition of an electron donor.

To our knowledge, this is the first in-situ field study of HCH degradation.

The bioscreen degrades HCH effectively and the same concept can be applied to other sites contaminated with insecticides and pesticides.

Keywords: Hexachlorocyclohexane, biodegradation, contaminated soil, groundwater treatment, active barrier, pilot test.

INTRODUCTION

The pollution of soil and groundwater with hexachlorocyclohexane (HCH) has caused serious environmental problems. Lindane (g-HCH) is the best known and effective insecticide component of HCH, and only 17% of HCH consists of this g-isomer. The remaining part consists of a-, ß- and d-HCH, which do not have insecticide activity. These isomers were separated from g-HCH, and dumped at waste sites resulting in polluted soil and groundwater. In contrast to a-, g- and d-HCH, ß-HCH was for a long time known as recalcitrant towards biodegradation under anaerobic and aerobic conditions (Bachmann et al. 1988a; Bachmann et al. 1988b). However, fundamental research has shown that ß-HCH can be microbiologically degraded to the intermediates monochlorobenzene (MCB) and benzene (B) under anaerobic conditions (Middeldorp et al. 1996; Van Eekert et al. 1998; Middeldorp et al. 2005). Complete mineralisation of all HCH isomers can thus be expected, as these intermediates can be biodegraded aerobically and some anaerobically. HCH biodegradation is summarised in Figure 1.

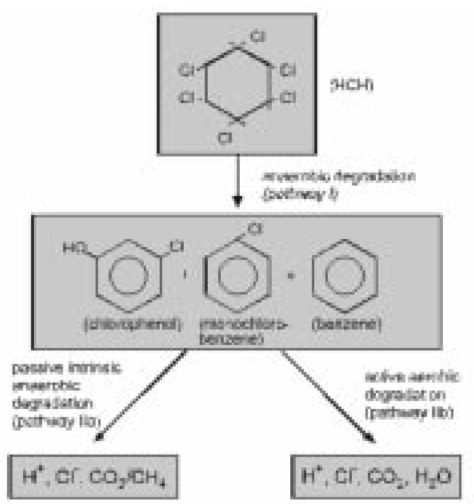

Figure 1: HCH biodegradation pathways

In this paper the feasibility of anaerobic and aerobic biodegradation of HCH and its intermediates will be discussed. Furthermore, the concept of a combined intrinsic and stimulated in situ bioremediation will be evaluated for HCH contaminated sites, using data obtained at an industrial site.

MATERIALS AND METHODS

Field characterisation. The geohydrological situation of the industrial site has been characterised previously (Langenhoff et al. 2002). Three defined sandy aquifers are defined down to a depth of 25 meters, and are separated by a peat-clay layer. The groundwater velocities are 7.5, 15 and 30-60 $m.yr^{-1}$ in the first, second and third aquifer, respectively. The groundwater direction (north-northeast) is towards a freshwater system (a canal), which forms the natural boundary of the site.

MCB and B were found as breakdown products of HCH in the core of the plume. In the first aquifer, benzene appears to be removed during downstream transport in the direction of the water system, whereas the monochlorobenzene concentration remained fairly constant. In the second aquifer, the concentration of MCB, and B showed no decline.

The redox potential characterisation of the source area of the first aquifer indicated sulphate reducing and methanogenic conditions. These low redox potential conditions are reported to be favourable for reductive dechlorination. In the downstream part of the plume, iron-reducing conditions are predominant. The redox conditions in the second aquifer were less clearly defined, but are characterised as reducing conditions.

Both aquifers showed an average DOC concentration of 27 $mg.l^{-1}$, indicating the presence of sufficient electron donor capacity for reductive dechlorination. Intermediates of the dechlorination process were found, indicating that intrinsic biodegradation of HCH does take place at this location. HCH has also been detected in an adjacent canal, indicating that the degradation processes are not fast enough to prevent the contamination of the canal with HCH

Biodegradation studies have shown that it is possible to stimulate HCH degradation to MCB and B through the addition of an electron donor and the degradation of MCB and B via aerobic degradation (Langenhoff et al. 2002). This concept was implemented at the industrial site, in conjunction with other redevelopment activities.

RESULTS AND DISCUSSION

At the industrial site, a container terminal is constructed at the border of the canal, forming the boundary of the site. This canal needs to be protected against HCH contamination, and therefore removal of HCH from the discharging groundwater is needed.

During the redevelopment of the site as a container terminal, infiltration facilities are installed to infiltrate elec-

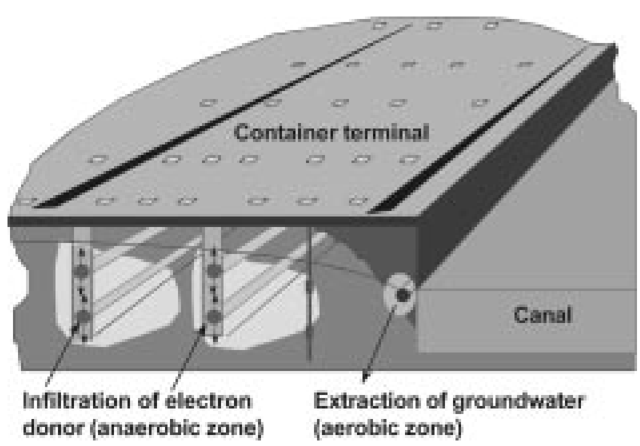

Figure 2: Design of the bioremediation system

tron donor to the groundwater to create an anaerobic infiltration (activated) zone in which the HCH can be transformed into MCB and B, see Figure 2.

Aerobic conditions are required for the degradation of MCB and B, therefore the anaerobic infiltration zone is followed by an aerobic step. At this site, the groundwater had to be extracted from the site, due to the presence of an impermeable sheet pile. The extracted groundwater is treated aerobically in a wastewater treatment plant on site.

The specific design of the system was determined by the integration of the bioremediation system and the redevelopment of the site as a container terminal.

The infiltration facilities were installed in 2001 and every three months an infiltration with methanol as electron donor was performed. The effect on the HCH degradation was monitored by measuring the concentrations of HCH, MCB and benzene in the extraction drain. The extraction drain is located 20 m downstream from the infiltration facilities, indicating that the effect of the infiltration is visible in the extraction with a delay of 4 to 8 months, due to the groundwater velocity of 30 to 60 m/yr.

The concentrations of HCH, MCB and benzene in the extraction drain are given in Figure 3.

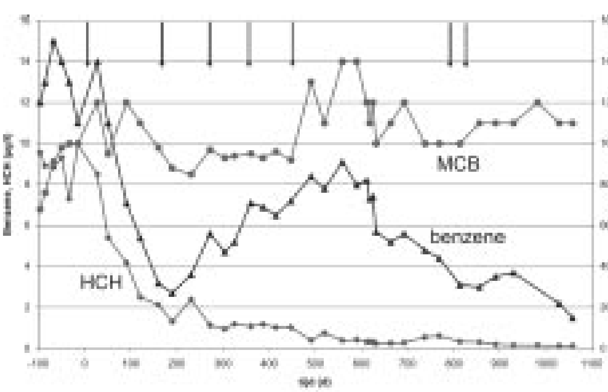

Figure 3: HCH, MCB and B concentration in the extraction drain at the industrial site. Arrows indicate infiltration with electron donor

Day -100 to day 0 indicate the concentrations in the extraction drain prior to the redevelopment of the site. The HCH, MCB and benzene concentrations have a level of about respectively 9, 100, and 14 µg/l. At day 0 (June 2001), the redevelopments at the site started and a concrete floor was installed. This decreased the concentration of HCH in the groundwater, as infiltration of rain and seepage water at the site stopped, which led to a decrease in desorption of HCH from soil particles. Less HCH was present in the groundwater, and the natural attenuation (degradation) of HCH into MCB and benzene stopped, resulting in a decrease in MCB and benzene concentration. At the same time, the infiltration was started, but its effect was seen in the extraction drain only after 6 months. As previously discussed, this is due to the location/position of the infiltration facilities and the extraction drain.

An increase in the concentration of the intermediates MCB and benzene was found, indicating that HCH was degraded. HCH was hardly detected in the groundwater, due to its desorption properties. HCH is adsorbed to the particles, dissolves and is immediately degraded into its intermediates.

After two years of intermitting infiltration, the infiltration was stopped to see its effect. This resulted in a decrease of benzene production from day 600 to 1100. The effect on the MCB concentration is less pronounced and might indicate that the formation of MCB from HCH is a chemical process and not a biological process. The infiltration was started again at day 850, but its effect is not yet visible in the extraction drain. A monitoring filter that is located near the infiltration filter showed increasing concentrations of MCB and benzene (results not shown).

CONCLUSION

At the industrial site, the site characterisation and the biodegradation studies showed that in the natural situation HCH is degraded into monochlorobenzene or benzene, but the degradation processes are not fast enough to prevent the contamination of a canal with HCH.

The field experiment has shown that the degradation process of HCH can be stimulated via the addition of an electron donor. Conclusive results show that the degradation of HCH is the result of the addition of an electron donor. To our knowledge, this is the first field study in which HCH is successfully degraded under anaerobic conditions.

The bioscreen degrades HCH effectively and the same concept can be applied to other sites contaminated with insecticides and pesticides.

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HEXACHLOROCYCLOHEXANE (HCH) RESIDUES IN INDIAN ENVIRONMENT: PROBLEMS AND SOLUTIONS

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HCH AS AN INSECTICIDE

1, 2, 3, 4,-5, 6- Hexachlorocyclohexane (HCH), a broad-spectrum insecticide, is one of the most extensively used organochlorine pesticides for the control of agricultural pests and against mosquitoes in malaria health programmes. The use of HCH has brought tremendous benefits to mankind by controlling agricultural pests and also by vector born diseases. However the extensive and indiscriminate use of HCH created a very serious environmental problem. The unusual process of its production has further aggravated the situation. At first (until 1970s) a mixture of HCH isomers (technical HCH) as a whole was applied, but since the late 1970s the active isomer (γ-HCH) was separated from other inactive isomers (α-, β- and δ-HCH) and the latter were discarded at waste sites. This secret of HCH contamination is not known to many.

SECRET OF HCH PRODUCTION

Hexachlorocyclohexane (HCH), a broad-spectrum insecticide, was one of the most extensively used organochlorine pesticides in India for the control of agricultural pests and against mosquitoes in malaria health program since 1950s. Until 1997 a complete mixture of HCH isomers (technical HCH) was used. Technical HCH is prepared by chlorination of benzene in the presence of UV, resulting in the formation of a mixture primarily containing the four isomers γ-HCH (10-12%), α-HCH (60-70%), β-HCH (5-12%), and δ-HCH (6-10%) (19). Of these, only γ-HCH (also known as lindane) has insecticidal properties. The purification of γ-HCH from rest of the isomers, extensive and widespread use of technical HCH, unregulated disposal, and the persistent nature of HCH isomers have created two types of contamination problems in India: (i) low levels of contamination of agricultural soils and groundwater, mainly caused by the intended usage, and (ii) high levels of contamination at the production sites caused by unregulated disposal of the non-insecticidal isomers α-, β- and δ-HCH (Prakash et al., 2004).

NON INSECTICIDAL HCH WASTE IS A SERIOUS GLOBAL PROBLEM

Although the use of HCH has been banned in number of countries and the ban has reduced the levels of HCH residues from agricultural soils over the years, the HCH dumping sites are now the main source of HCH contamination. HCH dumping sites are present in all over the world where HCH was manufactured. While such dumping sites have been discovered and reported from some countries like Netherland, Spain (Oliviera et al., 2003), Brazil (Osterreicher-Cunha et al., 2003) Germany (Kalbitz and Popp, 1999) and India (Prakash et al., 2004) in many countries such dump sites are yet to be brought to the notice of public. Many sites are being discovered from newly formed states of Eastern Europe (Tafaj, 2003).

HCH PRODUCTION STILL CONTINUES IN INDIA, CHINA AND ROMANIA

In India, HCH was banned in 1997 but the restricted use of lindane still continues. In India lindane formulations are registered for use in pharmaceutical products for control of head lice and scabies on people. It is also registered for use to control pests in cotton, sugarcane, pumpkin, cabbage, onion, apple, walnut, maize, okra, potato, tomato, cauliflower, radish, cucumber and beans.

India produced approximately 30,000 MT technical HCH every year for agricultural use before 1997. Total HCH produced from 1950 to 1997 was 14, 10, 000 MT. Although many industrial units that produced HCH have been closed, the total installed capacity of lindane production in India as of now is 1,300 tones per annum (tpa), with two companies producing, Kanoria Chemicals and Industries Ltd. (with a capacity of 1000 tone per annum) and India Pesticide Limited (with a capacity of 300 tone per annum). India has produced 5,387 tones of lindane between 1995 and 2005 (Fig. 1). Out of which 434.18 tones have been exported. According to the industry sources, 5-8% of the total lindane produced in the country is sold to the pharmaceutical companies in India, 25-30% is used by the industry for formulation and 15-20% is exported annually.

Although details are not available, unconfirmed reports indicate that in addition to India, Romania and China also continue to manufacture HCH.

If we take the official figures of total lindane production of approximately 5000 tons into account during the past 10 years, there should be 45000 tons of non insecticidal waste (α-, β- and δ-HCH) that should be produced. This waste appears to have been discarded in the open as shown in Fig. 2*a,b* creating more dump sites in addition to those which have not been located yet. Unless decontamination of these sites is done, the residues of HCH would continue to create serious problem for years to come.

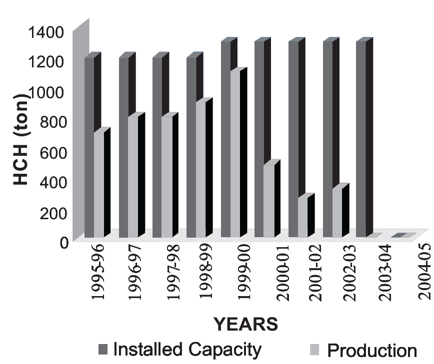

Fig 1. Installed capacity and production of Lindane in last 10 years
Source: Department of Chemicals and Petrochemicals Ministry of Chemicals and Director General of Foreign Trade (DGFT), New Delhi

Fig. 2a. Dump site not disclosed

Fig. 2b. Sealed Dumping site location not disclosed

DECONTAMINATION OF HCH WASTE

Current practices to detoxify HCH residues especially from dump sites rely on incineration, chemical treatments and landfills. These are economically restrictive. Bioremediation, the removal of HCH residues by the use of living organisms especially by bacteria while appears feasible but lot more work is needed to have a robust technology.

HCH DEGRADING MICROBES HAVE EVOLVED

Over the years, a number of microbes have been isolated from HCH contaminated sites. Interestingly, majority of the HCH degraders, isolated from India, Japan, France, Spain and Germany, have been found to belong to the group of sphingomonads (Sahu et al., 1990; Dogra et al., 2004; Böltner et al., 2005; Mohn et al., 2005). For the development of any bioremediation technology, availability of suitable microbes is the foremost essential requirement. We have been working with Sphingobium indicum B90A (formally known as Sphingomonas paucimobilis), a bacterium isolated from rice rhizosphere (Sahu et al., 1990) and capable of α-, β-, γ- and d-HCH degradation (Pal et al., 2005). Our study encompasses the biochemical, genetics and physiology of HCH degradation in this bacterium (Kumari et al., 2002; Dogra et al., 2004; Suar et al., 2004; Suar et al., 2005; Lal et al., 2006) with an aim to eventually use them for bioremediation . The catabolic genes associated with the degradation of HCH isomers were initially elucidated in Sphingobium japonicum UT26 and named as lin genes (Nagata et al., 1999). Subsequently, lin genes were found to be present in a majority of HCH degrading Sphingomonads (Kumari et al., 2002; Dogra et al., 2004; Boltner et al., 2005). Like UT26, the strain B90A (Kumari et al., 2002; Dogra et al., 2004) was also found to contain six structural genes, linA, linB, linC, linD, linE and linF and one regulatory gene (linR) leading to complete mineralization of γ-HCH. These genes were interestingly found to be associated with IS6100 (Table.1). The detailed genetic organization of these lin genes in Sphingobium indicum B90A has been studied and association of an insertion element, IS6100 (Dogra et al., 2004). The IS6100 (880 bp) element belongs to the IS6 family and has an extremely broad host range; the element has been found on the chromosome (Dogra et al., 2004), on plasmids (Hall, R. et al., 1994) and in (catabolic) transposons (Sundin and Bender, 1995). The lin genes showed a strange mosaic organization in all the Sphingomonads. The linA genes were flanked by a copy of IS6100 in B90A, Sp+ (Dogra et al., 2004) and three other isolates (DS3-1, a1-2 and a4-2) (Böltner et al., 2005). Similarly, linB gene was flanked by a copy of IS6100 in B90A and Sp+ (Dogra et al., 2004) from Germany and Spain (Boltner et al., 2005). linC gene apart from being located downstream to linA1 was also found to be flanked by two IS6100 copies in divergent orientation, possibly making a composite transposon in B90A (Dogra et al., 2004). Furthermore, linC is flanked by IS6100 upstream (5') in strain g1-7, downstream (3') in UT26 and on both sides in DS3-1. Similarly, linD gene was flanked by a copy of IS6100 in B90A (Dogra et al., 2004) ad Sp+. It was found that the stability of the lin genes is strongly influenced by IS6100 activity since deletion of lin genes were associated with the deletion of IS6100 copies in mutants of B90A and Sp+ (Dogra et al., 2004).

Our studies (Kumari et al., 2002, Dogra et al., 2004, Lal et al., 2006) have revealed amazingly high adaptability of Sphingomonads to HCH and interestingly lin genes were associated with IS6100 among all the Sphingomonads extraordinary role being played by IS6100 in the mobilization of these HCH degradative lin genes amongst all the HCH degrading Sphingomonads has also been revealed recently (Boltner et al., 2005). We have also studied the stability of the lin genes in Sphingobium indicum B90A and found that it is strongly influenced by IS6100 activity since deletion of lin genes were associated with the deletion of IS6100 copies in the mutants (Dogra et al., 2004). Our recent studies have revealed that lin genes are not uniformly distributed on the chromosome but are also present on plasmids in Sphingobium indicum B90A, Sphingobium japonicum UT26 and Sphingobium francense Sp+. Thus, IS6100 and plasmids (probably conjugative) appear to play a very significant role in HGT of lin genes among Sphingomonads a feature that is very suitable for the development of bioremediation technique through biostimulation.

The potential application of the aerobic bacterium Sphingobium indicum B90A, to achieve targeted degradation of all HCH isomers has been studied (Lal et al., unpublished). The conditions to cultivate strain Sphingobium indicum B90A on various substrates; including the very cheap substrate molasses have been studied. In addition, survival of B90A during storage on carrier material or whilst frozen, and its ability to remain active in degrading g-HCH in liquid culture, in soil microcosms and in soil contaminated with residual levels of technical grade HCH were determined. B90A grown on molasses and stored as frozen cell paste at –20°C retained almost 100% viability after 40 days. Both formulations (after 30 d of storage) were tested for their ability to degrade HCH in soil microcosms and in a small-scale field trial. Between 15-50% of lindane disappeared in microcosms inoculated with corncob powder immobilized B90A cells within 20 h of incubation at 30°C whereas 35% of lindane was degraded within 20 h in microcosms inoculated with B90A cells thawed from frozen batches. Small-scale field experiments have been conducted and two applications of corncob powder immobilized cells (at intervals of 10 days) resulted in complete disappearance of all but the β-HCH isomer, which was observed at 5% of its initial concentration. Overall, the studies conducted indicate that on-site aerobic bioremediation of HCH exploiting the biodegradative ability of Sphingobium indicum B90A, cultivated on molasses and stored and applied as immobilized on corncob powder can be a promising technology to clean-up HCH-contaminated soils.

With this back ground work on the molecular genetics of HCH degradation we believe strategies now can be designed to use this bacterium for bioremediation along with physical and chemical methods

FUTURE GOAL OF HCH RESEARCH

Focus of research should now shift to the identification of dump site, places with obsolete HCH and concerted efforts should be made to decontaminate HCH residues from these places. Efforts are also needed to develop cheaper and affordable technologies involving the use of physical and biological methods.

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USE OF WILD PLANTS FOR PHYTOREMEDITION OF KAZAKHSTAN SOILS POLLUTED WITH PESTICIDES

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ABSTRACT

In Kazakhstan, there is a deepening ecological crisis caused by contamination of the environment with obsolete and expired pesticides. Pesticide contamination is common on land surrounding destroyed warehouses that were part of the official plant protection service of the former Soviet Union. Pesticides and fertilizers were stored in these warehouses until 1990 when they were no longer maintained. These pesticide contaminated areas are called 'hot points'. Large-scale physical and chemical technologies for managing pesticide contaminated soils are expensive and unacceptable for Kazakhstan because of limited financial resources. One of the promising innovative technologies for managing pesticide contaminated soils is phytoremediation. Phytoremediation uses vegetation to accumulate, degrade, or stabilize environmental contaminants. We studied plant community structure at three 'hot points' locations in Almaty oblast. From these studies, 17 pesticide tolerant plant species were selected from plants that grew well in the center of the "hot points".

A greenhouse experiment using the pesticide tolerant species showed that certain plant species from wild populations have the ability to accumulate organochlorine pesticides and their metabolites (4,4-DDE, 2,4-DDD, 4,4-DDT, á-HCH, â-HCH and ã-HCH). The accumulation rate of organochlorine pesticides was found to be a specific characteristic of a plant species and dependent on the degree of soil contamination. Among the investigated species, seven accumulated metabolites of DDT and isomers of HCH in their tissues exceeding the MAC (Maximum Acceptable Concentration) by 80 times. These species were Artemisia annua, Erigeron ñanadensis, Xanthium strumarium, Kochia scoparia, Barbareae vulgaris, Kochia sieversiana, and Amaranthus tricolor. Six species exceeded the MAC by 10 times (Ambrosia artemisifolia, Solanum dulcamara, Artemisia absinthium, Medicago sativa cult, Aålgilops cylindrical,and Rumex confertus). Organochlorine pesticides taken up by the plants are distributed unevenly in different plant tissues. The main organ of organochlorine pesticide accumulation is the root system. This information can be used for technology development of phytoremediation of pesticide contaminated soils.

Key words: Pesticides, Phytoremediation, DDT, HCH, Kazakhstan

INTRODUCTION

Kazakhstan celebrated its independence from the former Soviet Union in 1991; however the impending environmental problems were not anticipated. Within five years of independence, pesticide storage warehouses from the official plant protection service of the former Soviet Union (called "Agrochemservice") were destroyed leaving the stored obsolete pesticides and their containers unattended and open to the environment. Most of the bulk pesticides have been moved to other storage areas, taken by citizens for individual use or resale in labeled or unlabeled containers, or released into the surrounding environment with no indication of their potential danger to local residents. However, people living around these warehouses use the land for pasture, kitchen gardens, play areas for children and a source of construction materials. In Kazakhstan, pollution of soil and water by obsolete pesticides is a serious ecological problem.

The areas of these former warehouses have become "hot points" or "hot spots" of contamination and represent a serious ecological danger. The largest former warehouses of "Agrochemservice" were located in Almaty and Akmolinsk oblasts because of the administrative importance of these areas and the level of agricultural development. Official data on the number of warehouses, their location, and the fate of the bulk pesticides are inconsistent. Two varying examples include one by Bismildin (1997), who states that there are 974 warehouses in Kazakhstan, of which 411 are in an emergency condition with an accumulation of 574 tons of pesticides and 54 thousand containers that have not been buried. In the second example, Nazhmetdinova (2001) states there are 1280 out-of-date warehouses in Kazakhstan and about 1 million tons of pesticides. Though the examples vary in quantification of pesticides, both illustrate there is an urgent need to remediate the soil and water around these "hot points" of contamination.

There are many different methods that can be used for remediation of pesticides in soil. Large scale and expensive remediation technologies that may be effective for pesticide contaminated soil and water are likely to be unacceptable in Kazakhstan due to limited finances and resources. Innovative natural remediation technologies like phytoremediation are promising if they can be shown to address cleanup requirements and can be effectively managed at an acceptable cost. Phytoremediation uses vegetation to accumulate, degrade, or stabilize environmental contaminants. This paper briefly summarizes the use of phytoremediation to reduce risk at hot points of soil contaminated with obsolete pesticides in Kazakhstan.

The purpose of this project was to develop feasible methods to reduce ecological and human health risk at obsolete pesticide sites using phytoremediation. In this paper the use of the term pesticide refers to the chloroorganic pesticide compounds that were analyzed which include: DDT, DDT metabolites (2,4 DDD; 4,4 DDD; 4,4 DDT; 4,4 DDE), and isomers of HCH (a- HCH; b- HCH; g- HCH). To investigate the potential use of phytoremediation, this project had four tasks including:

- Task 1- Field screening of several former obsolete pesticide storage warehouses (hot points) to characterize levels of soil contamination.
- Task 2 - Identification of pesticide tolerant plant species at hot points by surveys of plant community structure.
- Task 3 - Greenhouse fate and transport study using soil from hot points.
- Task 4 - Greenhouse and field plot studies to study the effect of fertilization on phytoremediation potential. (in progress)

METHODS

Task 1: Field screening of several former obsolete pesticide storage warehouses "hot points" to characterize levels of soil contamination

Five former warehouse sites (3 in the Almaty oblast and 2 in Akmolinsk oblast) were included in our initial study. This paper will only address the Almaty oblast, where soil samples from three former pesticide storage locations were taken to determine residual concentrations of chlororganic pesticides. The first point (Point 1) is located 15 km from Almaty with an area of 80 m^2. At Point 1, the destroyed foundation of the warehouse can be seen and local residents reside alongside the old warehouse. The second point (Point 2) is located 50 km away from Almaty with an area of 60 m^2. At point 2, the destroyed foundation can also be seen along with grazing cattle. White pesticide residuals lying on top of the soil and in the plants can also be seen and during certain time of the year smelled. The third point (Point 3) is located 36 km from Almaty. Point 3 is a concrete and asphalt platform with a total area of 100 m^2. Point 3 differs from Point 1 and 2 in that there were remnants of old pesticide containers found at this site.

Our study focused on the analysis of chlororganic pesticides as a marker for field contamination. Residual concentrations of chlororganic pesticides in soil and plant tissue was determined using standard methods adopted by the United States Environmental Protection Agency using a gas chromatograph (HP6890) equipped with an electron capture detector and a capillary column.

Based on history, we have assumed the "hot points" are chemically heterogeneous and contain, not only chlororganic pesticides, but probably other classes of pesticides and fertilizers. This is due to the use of former warehouses for storage of all chemicals used for plant protection and soil nutrient management. Soil sample analysis showed chlororganic pesticide contamination included DDT, DDT metabolites (2,4 DDD; 4,4 DDD; 4,4 DDT; 4,4 DDE), and isomers of HCH (a- HCH; b- HCH; g- HCH). Concentrations of these compounds exceeded limits of Kazakhstan's maximum acceptable concentration (MAC) (most of the chlororganic MACs are 100 ug/kg).

The most polluted point is 'hot point 2' where the concentrations of chloroorganic pesticides exceed the MAC by tens to thousands of times. Refer to Table I. Maximum pesticide concentrations of 4873 mg/kg for 4,4 DDT and 1797 mg/kg for 4,4 DDE were observed in soil samples collected from a depth of 0 to 20 cm. At the first hot point, the primary contaminants were 4,4 DDT and b-HCH. Soil concentrations exceeded MACs by 2.5 to 4.5 times. The maximal concentration of the DDT metabolites at point 1 was at the depth of 10 to 20 cm compared to 0 to 5 cm for isomers of HCH. Results for 'hot point 3' were similar to point 1.

The presence of a-HCH, 2,4 DDD and 4,4-DDD at hot points is of special concern according to normative standards for Kazakhstan, their presence in soil is not permitted The contents of a-HCH at all points varied from 1 to 301 mg/kg. Concentrations of 2,4-DDD ranged from 1 to 132 mg/kg, and of 4,4-DDD from 3 to 4873 mg/kg of soil. These data show the ecological danger of these areas also represent a significant potential risk to nearby populated areas.

Control soil samples were located at least 800 meters from each hot point. Control samples contained some metabolites of DDT and a-HCH. Metabolites of DDT primarily included 4,4-DDE and 4,4-DDT, but these did not exceed MACs.

Task 2: Identification of pesticide tolerant plant species at hot points by surveys of plant community structure

We studied plant community structure (referred to as phytocenosis in Russian) in areas surrounding each hot point to describe botanical diversity, to identify pesticide tolerant plant species that may be useful for phytoremediation, and to understand the mechanisms of detoxification of soil by plants. Tolerant species were identified by the Tahtadjan technique (1987). In the field, the following parameters of plant community structure were recorded: plant species, family, patchiness, vegetative coverage, frequency, and distribution. Additional parameters included: stratification of plant species with distance from the center of the hot point, phenological stages at different times during the growing season, and species vitality or vigor.

Genetic heterogeneity of plant populations growing at the hot points allowed us to identify likely pesticide tolerant species. At the first hot point, 75 plant species from 26 families were documented. At the second point, 83 species from 23 families, and at the third point, 87 species from 22 families were observed. Seventeen pesticide tolerant species were identified including: Artemisia annua, Artemisia absinthium, Agropyrom pectiboform, Artemisia proceraeformis, Amaranthus retroflexus, Ambrosia artemisiifolia, Barbareae vulgaris, Bromus tectorum, Erigeron ñanadensis, Êochia scoparia, Kochia sieversiana, Lactuca tatarica, Onopordon acanthium, Polygonum

Table 1. Concentrations of pesticides at three "hot points" in Almaty oblast. All concentrations are in mg/kg MAC refers to Maximum Acceptable Concentrations for Kazakhstan.

Sample	α- HCH	β-HCH	γ- HCH	4,4-DDE	2,4-DDD	4,4- DD	4,4- DDT
MAC	0	100	100	100	0	0	100
First point 1	21,0	182,0	10,0	15,5	0	4,5	15,0
First point 2	30,5	180,5	18,0	20,5	0	4,5	29,5
First point 3	**112,0**	269,0	**56,5**	55,5	0	30,5	206,0
First point 4	52,5	146,0	21,5	71,5	0	15,0	38,5
Second point 1	5,0	166,0	2,0	193,0	8,5	91,0	300,0
Second point 2	9,5	146,0	1,5	2160,0	**43,0**	60,5	194,0
Second point 3	15,5	**330,5**	3,5	204,0	28,5	71,0	382,0
Second point 4	10,0	154,0	2,0	**2733,0**	0	**295,0**	**1650,0**
Second point 5	13,0	234,0	2,5	2627,0	0	139,0	941,0
Second point 6	5,5	177,0	1,5	2107,0	0	39,5	220,5
Third point 1	< 1,0	111,5	< 1,0	180,0	6,5	7,5	79,5
Third point 2	2,5	120,0	< 1,0	56,5	0	0	13,0
Third point 3	3,0	132,5	7,0	460,0	7,0	16,5	112,0
Third point 4	1,0	114,0	< 1,0	98,0	0	4,0	37,5

aviculare, Rubus caesius, Rumex confertus, and Xanthium strumarium. Distinctive features of these species included relatively high vegetative cover near the center of the hot points. These species expressed high phenotypic plasticity (flexible expression of morphological characteristics) that suggests adaptation to pesticide contaminated conditions. These characteristics included plant height, root system development, root to shoot ratio, branching, color of leaves, and display of "gigantism" and "miniaturization" effects.

Task 3: Greenhouse fate and transport study using soil from hot points

Thirteen of seventeen pesticide tolerant species were used to study the fate and transport of pesticides in the soil and plant system in a greenhouse pot study. The experiment utilized soil from two former warehouse sites (hot points 1 and 2) to estimate the accumulative ability of plants that have naturally colonized an obsolete pesticide site. Control soil was collected from an uncontaminated region of Almaty. Sixteen species for hot point 1, sixteen species for hot point 2, and sixteen species for the control soil were planted in triplicate Thirteen of these species were available for analysis. Quantitative and qualitative content of HCH isomers and DDT metabolites were analyzed in soil, the plant root system, and aboveground plant tissue at the time of flowering.

The greenhouse trial established that variable pesticide concentrations can change plant growth, the rate of phenological development, peroxidase activity in roots and leaves, the ratio of the chlorophyll a to chlorophyll b, and alter evapotranspiration rates. Pesticides, as an anthropogenic factor, can inhibit photosynthesis, and as a growth hormone, can stimulate plant growth, affect speed of flowering and fruiting and change stress tolerance of an organism. These physiological and biochemical changes appear to demonstrate the level of adaptation of plants to pesticide contaminated soils. Therefore these characteristics can be used as biological indicators of stressful effects of obsolete pesticide contaminated soil.

Dissipation of pesticide contamination in soil likely occurs through numerous mechanisms including adsorption of pesticides to plant roots, translocations of pesticides in plant tissue, migration of pesticides through the soil structure, pesticide run-off by wind and water erosion, volatilization, photochemical decomposition, and biological decomposition.

In our greenhouse study, pesticide accumulation in 13 selected pesticide tolerant plant species depended on the initial level of pesticide contamination in soil and plant biomass production. The varying degree of pesticide accumulation appears to be a specific feature of plant species. Most pesticide accumulated is the root system; however, among the species we investigated, some species demonstrated capability to translocate pesticides from roots to above-ground tissues. These included Kochia scoparia, Artemisia annua, Barbarea vulgari, and Ambrosia artemisifolia.

Total pesticide accumulation for selected plant species varied with the highest, Xanthium strumarium, demonstrating pesticide accumulation from 296 to 78.4 µg. Other ranges of pesticide accumulation by plant species included: Artemisia annua (1 to 42.4 µg); Kochia scoparia (6.40 to 23 µg), Ambrosia artemisifolia (from 2.9 to 13.8 µg), Kochia sieversiana (from 1.9 up to 25.0 µg) and Solanum dulcamara (1.09 to 43 µg).

To help localize where accumulated pesticides are in the plant, histological analysis of plant tissue from a few species indicated pesticides were distributed unevenly within different plant tissues. If a species has a dorsiventral and isolateral leaf type then pesticides appear to collect in the palisade mesophyll. If it has homogeneous mesophyll then it collects in mesophyllous cells around conducting bunches. For example, Xanthium strumarium L. has a dorsiventral type of leaf; thus pesticides collect in the palisade mesophyll. In the stem, pesticides collect in walls of xylem cells. In root tissue, pesticides collect in parenchymous cells and xylem walls.

CONCLUSION

As a result of the field and greenhouse studies, plant species occurring at the former pesticide warehouses could be divided into 5 groups depending on the pattern of pesticide accumulation in plant tissues.

1. Pesticide accumulating plants: These are species in which the residual concentration of pesticides in plant tissues exceeds the MAC by at least ten times. Species in this category include: Xanthium strumarium, Kochia scoparia, Artemisia annua, and Kochia sieversiana.

2. Accumulators of HCH isomers. These are species in which the residual concentration of HCH isomers in plant tissues exceeds the MAC by 6 to 18 times. Four representatives of family Asteraceae are in this category including Artemisia annua, Ambrosia artemisifolia, Xanthium strumarium, and Erigeron canadensis.

3. Accumulators of metabolites 2, 4-DDD and a-HCH. These compounds do not have a maximum allowable concentration (MAC) for plants or soil. These species accumulate trace metabolites of DDT and a-HCH in plant tissues in which the residual concentration of pesticides exceeds the MAC for other compounds. These species include Ambrosia artemisifolia, Xanthium strumarium, Artemisia annua, Solanum dulcamara, Medicago sativa, and Barbarea vulgaris.

4. Pesticide accumulators capable of translocating pesticides from the root system to aboveground plant tissues. These are species, in which residual concentration of pesticides in aboveground tissues exceeds the MAC. They include: Kochia scoparia, Artemisia annua, Barbarea vulgari, and Ambrosia artemisifolia.

5. Non-accumulators. These are plant species that accumulate insignificant concentrations of pesticides in plant tissues. These species include Solanum dulcamara and Rumex confertus. They grow in the central zone of the “hot spots” in pesticide contaminated soil. These species may have practical value for development of phytoremediation technologies and should be investigated further for their ability to stabilize or enhance degradation of chlororganic pesticides in soil.

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A GROUNDWATER TREATMENT PLANT FOR REMEDIATION OF DDT, HALOGENATED ORGANICS, ARSENIC AND MERCURY AT THE LAGO MAGGIORE (NORTH ITALY)

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ABSTRACT

Over a long period of time DDT concentrations of up to approx. 3 µg/l (ppb), together with other chlorinated organics of approx. 4.2 mg/l (ppm) and iron compounds at a concentration of 2-10 mg/l (ppm), flowed from a former DDT production facility into the Lago Maggiore (North Italy). The pollutants, in particular DDT and its derivatives, concentrated in the sediments of the lake and contaminated fish.

By using a groundwater catchment system consisting of 31 wells, it was possible to collect the pollutants at their point of origin and to prevent their further contamination of the lake. No comparable remediation projects were/are known worldwide. Therefore the development of the plant configuration began at laboratory and pilot-scale plant before final implementation on industrial-scale.

The system combines a broad spectrum of process engineering by using three main modules: chemical process (flocculation/coagulation), physical process (stripping/desorption), and physio-chemical process (filtration, contact catalysis). Because of the large amounts of groundwater arising and the high porosity of the water-bearing layer, the total mechanical pumping capacity is approx. 850 m^3/h. The requested concentration limits to be met were set extremely low: DDT to 0.05 µg/l (ppb), chlorinated organics to 50 µg/l (ppb) and iron compounds to 0.05 mg/l (ppm). The required target values could be achieved directly from start-up. PRANTNER not only took on the process development, but also the complete construction, design, assembly and operation of the system.

INTRODUCTION

Pesticide production sites and the surrounding areas are often contaminated with considerable amounts of pesticides and their by-products. In addition, these sites can be polluted with a higher load of more volatile (often chlorinated) organics and in some cases are additionally impacted by toxic inorganic contaminants in effluents. The combination of contaminants makes each site unique and a challenge not only for the responsible authorities, but also for the engineering company tasked with the remediation.

The particular challenge to remediation and securing sites of this type and the area surrounding them is that, due to the complexity of pollutants, normally no single remediation technique can solve the problem. Rather, the mixture of toxins requires a combination of remediation technologies for

Figure 1: Groundwater treatment plant (850 m³/h) for remediation of DDT, chlorinated organics, arsenic and mercury

elimination of the whole range of pollutants. The protection of groundwater and receiving water catchment systems (rivers or lakes) is a key problem for this type of contaminated site. One of the largest groundwater remediation systems related to a pesticide production site was recently implemented and is now operated in northern Italy, close to the Lago Maggiore (Figure 1).

Over a long period of time DDT concentrations of up to approx. 3 µg/l (ppb), together with other chlorinated organics of approx. 4.2 mg/l (ppm), PAHs, iron compounds at a concentration of 2-10 mg/l (ppm) in combination with arsenic compounds and mercury, flowed from a former DDT production site into a river transporting them finally into the Lago Maggiore. The pollutants, in particular DDT and its derivatives (DDE and DDD), concentrated in the lake's sediments. Due to the high bioconcentration factor of DDT (Table 1) and derivatives these toxins accumulate in the food chain (biomagnification) from phytoplankton up to sea birds.

Table 1: Bio-concentration factors (BCF) of DDT for some aquatic organisms (5)

Aquatic organisms	BCF-value
Oyster	15000
Bream	12000
Other fishes	12000 - 40000

In 1996, high concentrations of up to more than 10 mg/kg (fresh weight) in cormorant and great crested grebe (1) were detected. Fish in the Lago Maggiore which serves as part of the area's food supplies were also heavily contaminated with DDT, up to several mg/kg of fresh weight, and therefore above both Italian and European limits (1). DDT and derivatives are endocrine disrupting chemicals and exhibit estrogenic activity (2-4). For the protection of human heath the Health Authorities in 1996 stopped fishing and eating of landlocked shad (Alosa fallax lacustris) and char (Salvelinus alpinus) in Switzerland, while in Italy the prohibition was extended to pollan (Coregonus sp.), whitefish (Coregonus macrophthalmus), rudd (Scardinius erythrophthalmus) and bleak (Alburnus alburnus alborella). These prohibitions are still in force. Furthermore it was decided to remediate the contaminated groundwater at source to prevent continuing contamination of the river and lake.

The paper presented reports on the technologies used for groundwater treatment in the former DDT production area for the whole range of pollutants in order to stop the chain of continuous run-off from the production site, contamination of the river and correspondingly the Lago Maggiore.

GROUNDWATER CATCHMENT AND OBJECTIVES SET BY AUTHORITIES

By using a groundwater catchment system consisting of four wells in the first stage (1998) and 31 wells in the second stage (2001), it was possible to collect the pollutants at their point of origin. Because of the large amounts of groundwater arising and the high porosity of the water-bearing layer, the total mechanical pumping capacity is approximately 850 m³/h.

The treatment plant must reduce the concentrations to the following, extremely low, boundaries defined by the responsible authorities (Table 2), before the water is returned to the aquifer.

Table 2: Required emission limits for contaminants in purified water

Contaminant	Required emission limit (µg/l (ppb))
DDT	< 0.05
Chlorinated organics	< 50
Iron compounds	< 50
Arsenic compounds	< 10
Mercury	< 1

The hydraulic boundary conditions were defined by the authorities as follows:

- Total extraction 350 m³/h (1st stage 1996), 850 m³/h (2nd stage 2001),
- Catchment at four wells (1st stage), 31 wells (2nd stage 2001)
- Direct return of treated water to river.

DDT ELIMINATION ON AN INDUSTRIAL SCALE

No comparable remediation projects are known worldwide, and thus no comparable process data could be used. Development of the final configuration began on a laboratory scale with inclusion of the known chemical properties of DDT/derivatives and other pollutants. After a short period of time, tests were carried out in a pilot-scale plant in order to be able to approach an industrial-scale operating process. With a scaled-down flow of 5m³/h both the interaction of the available groundwater in dynamic operation with the pilot plant and the results of laboratory batch testing were analysed to demonstrate the suitability of the processes planned.

A substantial part of the work during the development phase was invested into the determination and synchronisation of response times for the individual process modules (see below). Special complications were presented by the precipitation dependent fluctuations in the contaminant spectrum.

Based upon experience gained in the pilot tests at 5 m³/h, a multiple-street structure was proposed in order to be able to manage the scale-up to 350 m ³/h as quickly as possible and with the minimum of risk. The industrial scale plant was realised in 2 stages:

- First stage of development with four parallel streets; three streets 100 m³/h (equivalent to a scaling factor of approx. 20) and one street with 50 m³/h;
- Second stage of development with four streets, with 200 to 225 m³/h. (Figure 1).

Despite following the usual DIN regulations, at the beginning of the project there were no standardised testing procedures for water trace analysis of DDT at the low concentration range required that could provide both rapid and reliable results. In the context of a joint project with the analytical laboratories a reliable procedure was developed for the quantitative determination of DDT traces in water samples for concentrations of 30 ng/l and below.

TREATMENT

The preparation of the groundwater takes place in 3 stages with increasing elimination of the pollutants relative to their initial concentrations. The system combines a broad spectrum of process engineering technologies by using 3 main modules,

- Chemical process (flocculation/coagulation),
- Physical process (stripping/desorption), and
- Physio-chemical process (filtration, contact catalysis).

1. Flocculation / Coagulation; Filtration

The groundwater containing the dissolved organic contaminants (e.g. DDT and derivatives) or inorganic pollutants (e.g. iron, manganese or arsenic) is firstly dosed with the relevant chemicals (deferrisation module) to form barely soluble salts. Hydrophobic organic compounds adsorb on the relatively large and active surface of these salts.

The addition of specific substances (flocculants) allows the finely dispersed salts to coagulate and transform into a separable form. The separation takes place in a sedimentation tank

In this stage 90% of iron and 99% of arsenic is removed together with 90% of DDT and derivatives. The iron compounds in the polluted water are utilised for the removal of the arsenic by forming the barely soluble $FeAsO_4$ salt.

The remaining turbidity is finally removed from the water in multi-layered filters with support of catalytic deferrisation resulting in 99% elimination of Fe.

2. Desorption in stripping units/ adsorption

Stripping is a physical process for the removal of undesired contaminants with low/medium volatility from water into the gas phase. Packed Column Strippers where chosen as a robust and reliable technique. With this type of stripper, the water is spread evenly over column packing and falls to the bottom of the column. Air is blown countercurrent through the column. The column packing greatly increases the surface area available for desorption of the pollutant – and in this way influences the required height and amount of packing needed to reach the treatment targets. This type of stripper is most often used with substances that are easily strippable such as CHC (tetrachloroethene, tricholroethen, tetrachloromethane etc.) and mono-aromatic hydrocarbons (benzene, toluene, xylene). They have also been successfully used with less strippable substances such as methyl-tertiary-butyl-ether (MTBE) and tetrahydrofuran (THF) at atmospheric pressure.

99% of chlorinated organics were removed from the water phase in this stage. For the treatment of the loaded strip air two methods can be used:

- Catalytic destruction of contaminants in the strip air (5, 6)
- Adsorption of the loaded strip-air on to activated carbon

For the unit discussed, the customer specified adsorption on to activated carbon.

3. Activated carbon filtration

In the last treatment stage, the water was fed over an activated carbon filter. Prantner single pass activated carbon filters are used in many different applications. Activated carbon filtration has found broad acceptance, especially for easily adsorbed chlorinated and aromatic hydrocarbons (BTEX), as the standard process for treating contaminated water, as well as soil vapours and off-gases from stripping units. In particular, this process is popular for low and medium concentrations where it can be assumed that the filter capacity will not be exhausted quickly[1] .

This third remediation stage resulted in 99% elimination of DDT (and 99% elimination of PAH), thus reaching all required emission limits.

Impact of the water treatment plant on DDT contamination of the lake

The plant functions successfully and prohibits the in-flow of contaminants from the old production site to the river (and lake) during normal day-to-day operation. In October 2000, however, a heavy flood occurred and lake waters exceeded the maximum flooding level of about 2.5 m for 10 days, the highest levels for the entire 20th century. During this period DDT were transported from contaminated soils and river sediments to the lake. This was confirmed by the increase of DDT content in water and sediments in Baveno Bay and inflowing river after the chemical plant (8), and in another study comparing DDT concentrations in zebra mussel soft tissues at several sampling stations since 2001 with those collected at the same sampling stations in the preceding years (9). This revealed that the outline of the first plant with 400 m^3/h was too small for heavy rain events and one major reason for enlarging the plant to a capacity of 850 m^3/h in the second stage in 2001.

The study on zebra mussels also revealed that DDT in sediments of polluted parts of the lake (Baveno Bay (depth about 100 m)) is a depot for seasonal fluctuation of DDT concentrations and a reservoir for continuing contamination of other parts of the lake (9). Furthermore the river sediments also serve as a reservoir for DDT and derivatives (9) and will contribute to contaminating the lake for years to come. Up to now, no further interventions to confine chemicals and polluted soils or to drain the river bed have been taken (8). Therefore the effect of the described measures on the site is counteracted by the contamination reservoirs in the river and lake.

CONCLUSIONS

The required target values for the whole range of contaminants (DDT and derivatives, chlorinated organics, ar-

[1] For the adsorption of inorganic chemicals and compounds such as mercaptanes, a wide range of impregnated carbon is available. These are used when a mixture of organic and inorganic pollutants are present together.

senic, iron and mercury) could be achieved directly from start-up, even without the possibility of intermediate buffering of the treated water. In operation, concentrations were clearly under the regulation limits and in some cases even under the detection limit for the individual substance.

Owing to efficient project management, the short deadlines set by the client could be met and the plant could be realised within 11 months. PRANTNER not only took on the process development, but also the complete construction, design, assembly and operation of the system. The plant runs fully automatically and is equipped with PLC and process visualisation. Operating parameters can also be called up from a remote site via telemetry.

The overall positive effect of the successful treatment of the DDT contamination and other contaminants flowing to the lake in the unit described and the resulting knock-on effects, e.g. on fish and mussels, is lessened by the release of DDT and derivatives from reservoirs in river sediment and sediments in the lake. Bio monitoring measures (9) will have to be observed in the coming years before final conclusions on the success of these remedial actions can be drawn.

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TRANSFORMATION OF β- AND δ-HEXACHLOROCYCLOHEXANE BY *SPHINGOMONAS PAUCIMOBILIS* B90A

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Hexachlorocyclohexane (HCH) is a broad-spectrum insecticide that was extensively used worldwide since the 1940s. Technical HCH is a mixture of a (60-70%), β (5-12%), γ (10-15%), and δ (6-10%) isomers, whereby γ-HCH is the only isomer that shows insecticidal activity; all the other isomers are not insecticidal. The HCH isomers differ with respect to the relative orientation (Figure 1) of the chlorine atoms (axial or equatorial) bound to carbon atoms as well as with respect to physical chemical properties and persistence. However, all four isomers are considered to be highly toxic and recalcitrant pollutants worldwide. Although use of technical HCH has been banned in several countries, the restricted use of lindane (99% γ-HCH) continues and residues of all isomers are frequently being detected all over the world.

The purification of lindane from technical HCH for restricted use releases significant amounts of the other isomers as waste into the environment (Österreicher-Cunha et al., 2003).

Although the use of HCH has been discontinued, problems are surfacing now from former production and dump sites, in particular with the more stable α-HCH and β-HCH (Oliveira et al., 2003, Prakash et al., 2004). Several microorganisms (aerobic and anaerobic) have been reported to degrade HCH isomers. The aerobic degradation pathway for γ-HCH (Nagata et al., 1999) is well characterized, but little is known about the degradation pathways of the other

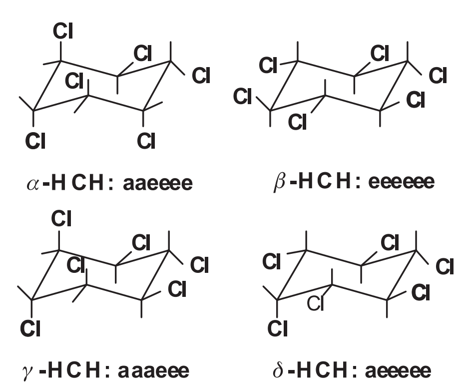

Figure 1: Structures and isomers of HCH showing respective axial (a) and equatorial (e) chlorine atoms

isomers. For development of future bioremediation strategies the knowledge and understanding of the metabolic and environmental fate of all isomers is essential for monitoring the degradation process.

The presence and the orientation of the chloro substituents determine enzymatic degradation and it is generally observed that γ-HCH (aaaeee) and α-HCH (aaeeee) are more easily degradable than δ-HCH (aeeeee) and β-HCH (eeeeee), as they have less equatorial chloro substituents. The anaerobic degradation pathway of β-HCH by an anaerobic bacterial coculture has been studied (Van Eckert et al., 1998, Middeldorp et al., 2005). Although a few aerobic bacteria able to degrade β- and δ-HCH have been recently isolated, the aerobic degradation pathway of those isomers has not intensively been studied and metabolites formed during transformation β- and δ-HCH have not been adequately characterized. Sphingomonas paucimobilis B90A (now classified as Sphingobium indicum B90A, Pal et al., 2005) is able to aerobically transform all HCH isomers including the more recalcitrant b- and d- isomers and is well characterized in terms of the organization of lin genes and dynamics of lin gene expression (Kumari et al., 2002, Dogra et al., 2004, Suar et al., 2004, Suar et al., 2005). In the present study, several metabolites were isolated from laboratory incubations of â- and ä-HCHs with the soil microorganism S. paucimobilis B90A.

S.paucimobilis B90A degraded α-, β-, γ- and δ-HCH within 24h ($\gamma > \alpha > \delta > \beta$) under aerobic conditions. However, mass balance calculations show incomplete mineralization of β- and δ-HCH. Several metabolites were isolated from the incubation mixtures. Two metabolites were formed from α-HCH and four metabolites were formed from β-HCH. By GC-MS analysis we could show that the metabolites were saturated and unsaturated chlorinated cyclohexanols and -diols. The study also revealed that equatorial-Cl in β- and δ-HCH were quite reactive toward hydroxylation by enzymes induced in S. paucimobilis B90A. This is in contrast to the generally accepted dehydrochlorination reactions of HCHs where axial-Cls are far more reactive. The exact structures and stereochemical configuration of the metabolites need yet to be elucidated.

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DEVELOPMENT OF THE TECHNOLOGY FOR BIOREMEDIATION OF SOILS, CONTAMINATED BY TOXIC CHEMICAL COMPOUNDS WITH THE HELP OF MICROORGANISMS-DEGRADERS

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1. INTRODUCTION

The pace of development of modern industry resulted in a vast anthropogenic pollution of the environment, which is a real menace of ecological crisis. In this connection, one of the primary tasks of the modern ecology is development of the most efficient methods of decontamination of hazardous industrial waste and purification of polluted territories.

Various methods for destruction and decontamination of solid and fluid industrial wastes and for cleaning of polluted soils from toxic hard-to-degrade compounds have been proposed. Physical, chemical and mechanical methods are predominant (burning, neutralization, adsorption, extraction, coagulation, ozonization, fast electron and UV irradiation, bituminous grouting and burial, mechanical collection, etc.). However, the available technologies are very energy and material consuming and, above all, not quite effective. Such cleaning yields great amounts of mud and by-products whose utilization causes serious ecological problems.

The analysis of progress trends in the study of environmental protection shows that, along with the improvement of the available physical and chemical methods, much attention is paid to biotechnological methods, which are recognized as undoubted priority by efficiency and economy. These methods are ecologically safe and compare favorably with other methods by the absence of secondary waste, because they allow a complete mineralization of chemical compounds discharged into the environment as industrial waste.

The degrading activity of microorganisms towards natural organic compounds, which enables the circulation of substances in the biosphere, is a basis of the biotechnological methods of environmental protection from technogenic pollution. The case with the circulation (mineralization) of unnatural compounds synthesized by modern chemical industry is much more difficult. Toxic chemicals, otherwise called xenobiotics, began to be intensively discharged into the environment not long ago (in the last 50 years). As a result of microevolution, microorganisms not only resistant to such chemicals but also capable of their degradation have appeared in the nature. These microorganisms may be a basis of biotechnologies for environmental protection and cleanup from different pollutants.

Bioremediation is the most efficient and ecologically safe method for cleaning of the environment from different pollutants. There are two fundamental approaches to biodegradation of xenobiotics in the natural environment: stimulation of aboriginal microflora by creation of the optimal conditions for its activity and introduction of effective microorganisms-degraders into a polluted ecosystem along with the addition of mineral salts.

The development of ecologically safe technologies is an up-to-date problem also for the program of CW destruction in accordance with the Chemical Weapons Convention. Russia has accepted the conception of a two-step destruction of chemical warfare agents, which envisages their chemical detoxification at the first step followed by destruction of the formed reaction solutions at the second step. The reaction solutions, although do not possess the toxicity of the initial chemical warfare agents, contain substances of the 2nd and 3rd classes of toxicity, which are not subject to discharge into the environment.

The current methods of decontamination of soils polluted by ecotoxicant, which include a number of sequential procedures (excavation followed by thermal treatment of soil, delivery of new soil and recovery of fertility), are very energy consuming, whereas bioremediation reduces the cost of this procedure approximately 1000-fold. A method of phytoremediation of soils polluted with mustard detoxification products has been developed by now. This method uses a number of plants, which are able to accumulate sulfur-containing compounds from soil and thereby to reduce their content 3-5-fold without treatment and 20-25-fold at additional treatment of such plantations with phytohormone solutions (Zakharova et al., 2000). Introduction of microorganisms capable of bioutilization or transformation of chemical warfare agents and their detoxification products into such soils may increase the cleanup efficiency tenfold, exposing these substances to a complete mineralization or transformation into less toxic compounds.

The search of microorganisms, which are able to utilize TDG, the non-chlorinated product of mustard hydrolysis, with a rather stable C-S bond (Harvey et al., 1998), is in progress.

One of the most important problems is development of an ecologically safe technology of the cleanup and bioremediation of soils polluted with POs. They include methylphosphonic acid (MPA), which is in the list of precursors for the synthesis of neurotoxic CW agents and is subject to destruction in accordance with the Chemical Weapons Convention. Intensive pollution of the environment with POs is a result of a wide and uncontrollable use in agriculture of a number of pesticides, herbicides, and insecticides. At present, the most significant problem in purification of the environment from POs is the degradation of POs with a hard-to-hydrolyze direct C-P bond. This bond is resistant to photolysis, chemical hydrolysis, thermal degradation, and occurs in a wide range of both natural and anthropogenic POs (MPA and its analogs, glyphosate or “round-up”, phosphonolipids, methylphosphonylfluoride, etc.).

Destruction of POs and remediation of contaminated territories involve physical, chemical and biological methods. Biological technologies are the most preferable due to ecological safety, low cost of work, and rather high efficiency, which has been more than once demonstrated at solution of other ecological problems (Zharikov et al., 2000; Boronin et al., 1997).

The ability to utilize POs with the direct C-P bond as a sole phosphorus source has been known for a comparatively long time. The biocatalytic methods for detoxification of organophosphorus CW by uncoupling of P-O and P-F bonds using organophosphate hydrolase have been developed (Zhang et a., 1999, Dave et al., 1993). Microorganisms possessing high activity of C-P lyase, which splits the C-P bond of MPA and its analogs (the products of enzyme-based hydrolysis of neurotoxic CW agents – sarin and soman), were revealed (Yakovleva et al., 1998), but their activity was very low.

2. RESULTS AND DISCUSSION

The State Institute “Research Center for Toxicology and Hygienic Regulation of Biopreparations” (RCT&HRB) was created by the order of the State Committee of the Russian Federation for Management of Property in 1993.

The RCT&HRB is head state scientific, methodical and expert establishment in the Russian Federation in the field of toxicological (pre–clinical) trials of recently developed preparations, including medical ones and it is a part of Federal Medical and Biologic Agency of Russia.

Specialists of the Department for Ecological Biotechnology carry out experiments in the area of ecology, including: development of the technology for bioremediation of soils, contaminated by toxic chemical compounds, utilization of organic agricultural and industrial wastes, biotesting of an environment, creation of combined forms of biohumus protecting plants from root rots.

Since 1996 we have been working with The International Science and Technology Center (ISTC). Project #228 on development of ecological safety technology for bioremediation of soils contaminated by polychlorinated biphenyls (PCB) has successfully completed. New strains of microorganisms–degraders are isolated. They are deposited in the international collection of microorganisms, on them international patent PCT applications are issued. Under the ISTC # 2093 project in Serpukhov on the area in 2 hectares the demonstration field tests of the developed technology that have shown an opportunity of its use in an expert have been conducted.

In our opinion biotechnologies have a number of advantages before physical and chemical methods: ecological safety, low cost and labour input. After bioremediation soil keeps its properties and fertility.

On the ISTC # 1892 project the technology for bioremediation of soils, contaminated by phosphoro-organic compounds with the help of microorganisms–degraders is developing. Participating institutions: The Research Center for Toxicology and Hygienic Regulation of Biopreparations (RCT&HRB), Skryabin Institute of Biochemistry and Physiology of Microorganisms at the Russian Academy of Sciences (IBPM RAS).

Presently the most topical problem is decomposition of phosphorus-organic compounds with hardly hydrolysable direct C-P bond. This bond is resistant to photolysis, chemical hydrolysis, thermal destruction, and is found in a wide range of phosphorus-organic compounds (methylphosphonic acid and its analogues, glyphosate or round-up, phosphonolipids, methylphosphonyldiphtorid, etc.).

<u>The goal of the # 1892 project:</u> search and selection of highly active strains of microorganisms–degraders of POC, isolation and study of the enzyme degrading direct Ñ-Ð bond and development on this basis of the technology for remediation of contaminated soils in situ.

Project tasks include:

• Isolation of microorganisms–degraders of POC degrading of direct Ñ-Ð bond from pure cultures.

• Identification and characterization of C-P lyase complex, identification of its composition and localization.

• Laboratory studies of Pn degradation by microorganisms-degraders and their acellular complex of C-P lyase

• Field studies of the efficiency of microbial degradation of Ðn in contaminated soils

• Experimental study of general toxic effect of promising strains-degraders and of soils contaminated by Pn before and after bioremediation on laboratory animals.

• Toxicological and ecological assessment of biotechnology for remediation of soils based on the application of microorganisms-degraders or C-P lyase complex.

At present soil sampling was performed on the territory of Moscow and Saratov Region, Krasnodar Territory. The sampling was performed in the vicinity of pest-killers storages, on the territories, contaminated with phosphoroorganic compounds, as in the soil, contaminated due to the activity of these pollutants, natural selection of the microorganisms, capable of decomposing Pn, has taken place for many years. In total, there were obtained more than 20 soil samples.

Research works on isolation of mixed and pure microorganism cultures, capable of decomposing Pn with direct C-P bond are carrying out. The isolation was performed out of accumulating (rich) nutria media and minimum saline nutria media, where the only source of carbon was represented by different concentrations of glyphosate (roundup) and methylphosphoric acid. All in total 39 natural isolates of microorganisms-degraders of Pn were isolated. The collection of microorganisms – Pn degraders was organized. The research work on optimization of storage conditions and microorganisms strains handling in laboratory environment is carried out. Screening with the aim of reception highly active strains of microorganisms, capable to decompose POC in the liquid medium and in soil is conducted.

Activity of isolated microorganism strains was assessed by the amount of produced biomass as well as by specific growth velocity on the media with mentioned above sources of phosphorus and glutamate as a carbon source. As a result, most active bacteria strains, growing with maximal specific velocity 0.12-0.15 hour^{-1} and producing biomass 2.0 - 2.5 g/l were selected.

Determined was PO_S concentration effect on growth of selection cultures and efficacy of biodegradation. It was shown that at initial concentration of carbon source in the medium (glutamate) amounting to 10 g/l, phosphorus utilization level lowers from 95 to 33% along with increase of MPA concentration from 0.05 up to 0.5 g/l (correlation C:P 247:1 – 24.7:1).

High concentrations of MPA and glyphosate (up to 10 g/l) do not inhibit growth of bacterial cultures. Under the same concentration of carbon source (10 g/l) and with increase of MPA concentration from 0.5 g/l up to 10 g/l, growing biomass amount increases from 1.9 to 3.7 g/l. At that, specific growth velocity lowers from 0.13-0.15 hour $^{-1}$ down to 0.1 hour $^{-1}$, and lag phase considerably increases (from 4 to 24 hours). The limiting factor for bacteria growth is exhaust of carbon. Introduction of 10 g/l of glutamate in the stationary phase at initial MPA concentration 2.0 and 5.0 g/l leads to increase of biomass 1.7-2.0 times, though specific growth velocity falls down to 0.017 hour $^{-1}$ comparing with 0.1 hour $^{-1}$ at the beginning of cultivation, what seems to be consequent to oxygen limitation when the biomass is large.

Studying of gas phase composition by gas chromatography method at bacteria cultivation in aerobe conditions showed presence of methane in it. Culture activity was 400 nanomole CH_4 /g of biomass/day, and substrate utilization level was 83.2 % during 96 hours. Detection of methane and non-organic phosphate testifies to that MPA degradation in the bacteria under studying is realized by C-P lyase at the expense of breaking of direct C-P bond.

The work on detection and characterization of microbial enzyme of C–P lyase has been started. The results of biochemical studies on isolation and study of C–P lyase properties will allow to adjust the process of PO_S degradation and, thus, to influence contaminated soils remediation efficiency.

Laboratory and field trials results will be used to develop bioremediation technology for soils contaminated by toxic phosphorus-organic compounds, based on in situ application of microorganisms-degraders or their enzyme preparations.

The ISTC # 2488 project concerns with development of the technology for microbial bioremediation of soils contaminated by poisoning mustard gas. Participating institutions: The Research Center for Toxicology and Hygienic Regulation of Biopreparations (RCT&HRB), Scientific Research Center for Ecological Safety of the Russian Academy of Sciences (SRCES RAS).

<u>The goal of the ISTC # 2488 project</u> is search of natural strains of microorganisms–mustard gas degraders and development of technology for bioremediation of soils on their base.

Project tasks include

- Isolation and selection of pure cultures of microorganisms - PMGH degraders from the environment
- Carrying out laboratory investigations of destruction of PMGH by microorganisms
- Determination of directivity of PMGH inhibiting effect on microorganisms-degraders
- Determination of main biochemical stages of partial and complete destruction of PMGH by microorganisms–degraders
- Conducting field experiments on soil bioremediation contaminated by PMCH with the help of microorganisms–degraders
- Toxicological assessment of isolated strains–degraders.

Microorganisms were isolated from soil of different regions of Russia contaminated by chlororganic compounds (pesticides, chemical weed-killers) for a long time and from the silt on sites of chemical weapon (including mustard gas) dumping in the Baltic Sea.

Laboratory studies on microbial destruction were carried out on soils contaminated by PMGH. These substances are generated in places of storage and liquidation of chemical weapons. PMGH are mixtures of thiodiglycol (TDG) and products of its non-complete dechlorination with hydrochloric acid – chloroorganic compounds (COC).

During laboratory studies, 136 microorganism isolates were obtained from natural microorganisms isolates. Of them, 19 strains able to degrade PMGH fully or partially were selected during the screening. The result of laboratory tests showed that strains have various degrading properties.

Basic catabolism reactions of thiodiglycol (main product of mustard gas and PMGH hydrolysis) are oxidation to TDGA followed by breaking of C - S bond in TDGA and TGK molecules with acetate production, which is involved in reactions of central metabolic ways to provide cells with carbon and energy sources.

A critical moment in the development of the bioremediation technology is study of the industrial use potential of the microorganisms isolated from industrial and technogenic areas. It is important to be certain that the indicated microorganisms –degraders are harmless for the personnel working with them. Microorganisms must be non-toxic and not cause diseases at any routes of getting into human body.

RCT&HRB has the vivarium complex which equipped under international requirements GLP. Assessment of the strains' harmlessness was performed on laboratory outbred white mice rats. Study of pathogenic properties of strains was performed in compliance with International requirements regarding the following indices:

- average lethal dose (LD_{50});
- toxicity;
- toxigenicity;
- dissemination of strains in internal organs of experimental animals.

As a result of toxicological trails, 7 strains of microorganisms– PMGH degraders safety for worm blooded animals and suitable for using at soil bioremediation were selected.

The RCT&HRB conducted small-scale field-testing on bioremediation of soils contaminated by PMGH with the use of microorganisms-degraders. Testing is being performed on a dedicated site. PMGH was added into the soil on the basis of 500 ml / m^2. Results of chemical analysis showed that concentration of TDG in soil is 840 mg/kg, but COC concentration – 680 mg/kg. Study goals: study of degrading ability of 2 chosen strains- MGHP degraders in field environment; study of soil bioremediation processes by means of chemical-analytical methods, biotesting on animals-biotests, microbiological and biochemical studies; study of general toxic effect of water extracts of PMGH-contaminated soils on laboratory animals (white rats) before and after bioremediation.

As received data have shown that the type of soil and its chemical structure – in particular content of organic substances and concentration of humic acids has the great effect on the bioremediation processes. In soil "rich" with nutrients there are both processes of natural PMGH destruction, and processes of microbial bioremediation more intensively.

For 1 month of microbial bioremediation 100% TDG degradation was observed and 91-94% COC degradation.

Biotesting on Daphnia has shown, that during microbial PMGH decomposition ПГИ integrated toxicity of soil gradually decreases from 80 % up to 3 - 12 %, reaching a safe level. Thus decrease of integrated toxicity in soil well correlates with decrease of TDG and COC concentration in soil. Experiments on warm-blooded laboratory animals have shown, that soil after bioremediation is not toxic. Hence, during the microbial bioremediation of soil it is not formed toxic products of TDG degradation.

PMGH introduction in soil and its treatment with strains–degraders did not cause suppression of viability of native soil microflora. Authentic decrease of dehydrogenated activity of soil contaminated by PCB in comparison with the control at the beginning and for 14 day of field experiment is established. The tendency of restoration dehydrogenated activity for soil on the sites cultivated by microorganisms is noted.

At the beginning of the experiment PMGH had the expressed toxicity in relation to oats germ. The length of rootlets and tops of oats germ was in 1,2 - 2 times less, than in the control. During the bioremediation the phytotoxicity of soil decreased to a safe level.

Results of laboratory and field tests have shown, that during microbial bioremediation of soils contaminated by PCB, there is a weeding from toxic compounds. The developed biotechnology is ecologically safe.

3. CONCLUSION

1. Possibility for biodegradation of detoxification products of mustard gas, neurotoxic CW agents – sarin and soman, and organophosphorus herbicides using microorganisms isolated from the areas polluted with these substances and adapted to their bioutilization has been shown.

2. The pathway of metabolism of TDG, the product of mustard gas hydrolysis, utilized by microorganisms as a carbon source – has been established and the conditions of the highest efficiency of TDG biodegradation have been determined.

3. The cultures of microorganisms degrading methylphosphonic acid via the uncoupling of direct C-P bond have been isolated and selected. The efficiency of biodegradation is to a great extent determined by C:P ratio in the medium and by concentration of organophosphorus substrates.

4. Selected active strains-degraders can be used as a basis of biopreparations in the technologies for remediation of soils polluted with the products of CW agents detoxification and organophosphorus herbicides.

Thus, microbiological bioremediation it is possible to recommend for detoxication of soils contaminated by products of decomposition of the chemical weapons.

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BIOTECHNOLOGICAL ASPECTS OF ECOLOGICALLY PURE PESTICIDE-FREE FOODSTUFF PRODUCTION

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Special concern of those who are involved in agricultural production is provision of high food value and marketability of fruits, berries, corn, potato and vegetables.

The real way to tackle the problem is the development and introduction of novel, highly productive, ecologically sound biopreparations to be applied when producing the products, certificated as “ecologically safe”.

In Russia since the 70-th, years industrial production of biological preparations as the means of protection of plants from harmful insects and diseases is carried out. If compared with chemical insecticides, the biological products feature the selectivity of action. Biological products easily decay in ground, in water, and under action of solar beams, do not cause acquired tolerance of insects to them as distinct from chemical preparations.

In comparison with chemical protective means biopreparations have an effect only on certain species and groups of insects. When biopreparations act on a caterpillar larva they kill the insect in a few days. These biopreparations are non-toxic for man, animals or fish as well as for useful insects.

In Russia it is feasible to provide the industrial-scale production of such biological products as: insecticides, fungicides, biofertilizers and growth factors. Rate of the insecticides and fungicides application comprises from 0.2 up to 1.0 kg/ha depending on a kind of insects, their number, weather conditions and the equipment. Growth factors based on endophytic fungi-simbionts is a new direction. They are very effective and technologically effective. Rate of their application is 1-2 ml/ha. The most popular preparations are the following:

BICOL

Is especially effective against larva of potato beetles, caterpillar, cabbage moth, beet webworms, codling moth, black-veined, fall webworm, leaf-rolling moth, American tent, gypsy, abraxas, grossulariata, etc.

Bicol is applicable for the following plants: potato, tomato, pepper, cabbage, beet, carrot, apple-tree, pear-tree, plum-tree, sweet cherry, apricot-tree, mulberry-tree, gooseberry, pyrethrum, eglantine, valerian, calendula, hop cucumber, etc.

BAXIN

Is an effective biological preparation which suppresses the growth of more than 100 species of different leaf-cutting caterpillars on the following plants: beet, carrot, cabbage, apple, pear, plum, cherry, sweet, apricot, mulberry -tree, currant, gooseberry, vine, hog and flowers.

Baxin is manufactured in a form of concentrated dry powder which should be watered before use.

LUTAN

Is very effective against different species of injurious fungi. This preparation can be applied for plants growing in fields and greenhouses and for preserving fruits and vegetables during transportation and storage.

Lutan is manufactured in a form of concentrated paste.

NIKFAN

The producer of the preparation is endophytic fungi-simbionts, isolated from various parts of plants. Due to its high biological activity, the preparations of “NIKFAN” type (symbiont) can be used for pre-seeding treatment of seeds and vegetative mass in process of growth as immunomodulators and the sources of phytohormones. Owing to such combined effect they provide the increase of seed germination; promote the grafting; enhance resistance of plants to adverse growth conditions; activate root-formation and photosynthesis; enhance frost- and drought-resistance; reduce the terms of ripening; increase the efficiency of mineral fertilizers’ application; decrease the content of nitrates, heavy metals and radionucleids in plants. As a result, the crop yields increase by 10-30 %. The last experimental data show an accumulation of the selenium in the tubers. This offers the opportunity to use these products as a material for curative and prophylactic nutration.

Last experimental data show accumulation of selenium in tubers of plants. It gives prospect for use of products as raw material for a treatment-and-prophylactic feed. Thanks to such complex effect they provide:

- the increase of seed germination for 10-15 %;
- promote the grafting;
- enhance resistance of plants to unfavorable growth conditions;
- activate root-formation and photosynthesis;
- enhance frost- and drought-resistance;
- reduce the terms of ripening for 1-1.5 weeks;
- increase the efficiency of mineral fertilizers’ application;
- decrease the content of nitrates, heavy metals and radionucleids in plants.

Due to this the crop yields is increasing for 20-50 %.

The biological product concerns to 4 class, is practically harmless to the person and animals. The preparation is hi-tech. It is supposed to use the preparation in the amount of 1~3 ml per hectare.

We illustrate article the following photos.

Photos 1, 2, 3, 4 and 5: Experimental plants

THEME V: HEALTH RISKS ASSESSMENT BY OBSOLETE PESTICIDES

SOIL-PLANT TRANSFER OF ORGANIC CHEMICALS AND DERIVATION OF TRIGGER VALUES

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INTRODUCTION

The Federal Soil Protection Act [Anonymus, 1998] has been put into practice by the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) of July 12th, 1999 [Anonymus, 1999a]. Precautionary values and trigger values as laid down in the Law[1] are an important instrument to realise its requirements. Trigger values are related to various soil uses and objectives of protection, which are „human health“, „quality of food and feed“, and „leachate to groundwater“.

The exact procedure to obtain trigger values for „quality of food and feed“, which has to consider the soil-plant transfer of chemicals for soils under agricultural use and household gardens, is laid down in the Federal Bulletin No. 161a [Anonymus, 1999b]. It can be summarized by:

– consideration of maximum residue levels in/on plants
– quantitative description of soil-plant transfer and derivation of a maximum acceptable soil content
– plausibility check
– final stipulation of trigger values.

It is within the scope of the paper to give a description on the methodology of trigger value derivation, to present soil-plant transfer coefficients for several organic compounds obtained by outdoor lysimeter experiments, and to present a suggestion for the trigger of hexachlorobenzene.

[1] § 8 Federal Soil Protection Act: Precautionary values: “soil values which, if exceeded, shall normally mean there is reason that concern for a harmful soil change exists, taking geogenic or wide-spread, settlement-related pollutant concentrations into account”
Trigger values: “values which, if exceeded, shall mean that investigation with respect to the individual case in question is required, taking the relevant soil use into account, to determine whether a harmful soil change or site contamination exists.”

MATERIALS AND METHODS

1. Methodology of trigger value derivation

1.1. Target: quality of food

1. Step: Consideration of maximum residue levels in/on plants

Trigger values are calculated by inclusion of maximum residue levels (MRL-levels, „Rückstandshöchstmengenverordnung“ of 21.10.1999, modified on 20.11.2000) and ADI-values, respectively. In case these official values have not been derived for the compound under consideration a preliminary MRL´-value is assessed using N(L)OAEL-values and additionally applying a safety factor ($SF_{toxicological\ reference}$). In case none of the toxicologically relevant data is available the soil trigger value cannot be derived.

2. Step: quantitative description of soil-plant transfer and derivation of a maximum acceptable soil content

The soil-plant transfer coefficient is defined as the quotient of the substance content in the respective plant compartment (given in dry weight) and the soil content (also given in dry weight):

$$f_{transfer\ (i)} = \frac{C_{plant\ (i)}\ [mg/kg\ dm]}{C_{soil}\ [mg/kg\ dm]}$$

Since the soil-plant transfer depends on both, soil and plant properties, ideally each food item and all representative soils should be tested. However, such a broad variety of experimental studies is not achievable and thus, the following assumptions and definitions were applied:

– The ideal data set is characterised by five soils and ten representative food items. As long as a heterogeneous data base is available with information, which is difficult to interpret, the five soils / ten food items data base is considered to be the optimum. In case systematic studies are published, a data set characterised by three soils and six food items is considered to be sufficient.

– In case the optimal soil data set is not available a safety factor (SF_{soil}) is applied to the mean transfer coefficient for each food item.

– The experimentally determined transfer coefficients for the individual food items each are combined and a mean is calculated.

The maximum tolerable soil content is, in a first step, calculated separately for each tested food item by using one of the alternative equations depending on the availability of MRL- and ADI-value, respectively.

In case MRL-values are available the equation is:

$$\text{maximum tolerable soil content (i) [mg/kg dm]} = \frac{HF \times MRL\ (i)\ [mg/kg\ ww]}{f_{transfer\ (i)}\ [1 - (\text{water content}\ [\%] / 100)]}$$

with:

i = vegetable food (i)

MRL = maximum residue level [mg/kg wet weight]
$f_{transfer(i)}$ = mean of transfer coefficients for food item (i)
HF = hazard factor according to approach "toxicological hazard assessment of chemicals" [Anonymus, 1999c].

In case no MRL-value is available the equation is:

$$\text{maximum tolerable soil content (i) [mg/kg dm]} = \frac{\text{HF x MRL´ (i) [mg/kg ww]}}{f_{\text{transfer (i)}}\,[1 - (\text{water content [\%]} / 100)]}$$

where MRL´ is:

$$\text{MRL´ (i) [mg/kg]} = \frac{\text{ADI [mg/kg bw d] x 20 kg x portion (i) in food basket}}{\text{daily intake (i) [mg/kg]}}$$

with:
ADI = acceptable daily intake
20 kg = reference for daily intake: girl, 4-6 years of age, sensitive subgroup, weight 20 kg

The finally proposed maximum tolerable soil content, which is the basis for a plausibility check and expert-judgment, is identical with the lowest value out of the ensemble of calculated maximum tolerable soil contents for the individual food items. In case not all of the ten food items have been tested, again safety factors ($SF_{food\ item}$) are applied.

The finally proposed maximum tolerable soil content is multiplied with a so called „hazard factor"(HF). Maximum residue levels are derived as precautionary values. Food with residues below these levels should not cause adverse health effects for all population groups including sensitive subgroups such as children. However, the maximum tolerable soil content – in the sense of a trigger value - does not reflect the precautionary principle but the avoidance of hazard to human health. Thus, a hazard factor is added. The use of such a „hazard factor" is in accordance with the derivation of soil trigger values for the objective of protection „human health, direct soil contact" as published in the Federal Bulletin No. 161a.

3. Step: plausibility check
and
4. Step: final stipulation of trigger values

The finally calculated maximum tolerable soil content is subjected to a plausibility check. The check comprises – among others – a comparison with background values and precautionary values in order to make the trigger values operable. Finally, the suggested triggers are stipulated in the course of a moderated round table discussion including expert-judgement.

b) Objective of protection: quality of feed

For the derivation of maximum tolerable soil contents for the objective of protection „quality of feed" the procedure as laid down in the Federal Bulletin No. 161a is followed:

– grassland and soil under agricultural use (for maize) are treated identically.

– The legal basis for maximum tolerable plant levels is Directive (29/99/EEC) as well as the German „Futtermittelverordnung"

– The Directive (29/99/EEC) gives maximum tolerable plant levels for aldrin, DDT, HCB, HCHs and dioxins without differentiating between feed items.

– For other than these compounds or compound groups the maximum tolerable soil content currently cannot be derived.

2. Outdoor Lysimeter Experiments

2.1. Design of Lysimeters

The inner surfaces of the lysimeters (1 x 1 m surface area and 0,75 m depth) were coated by stainless steel. The lysimeters were equipped with a leachate outlet and filled by a 5 cm drainage layer, a 35 cm subsoil layer and a 35 cm upper soil layer, the latter having been spiked with the substance under investigation. The leachate was collected and analysed for contaminants.

2.2. Application of contaminants and cultivation of lysimeters

The substances under consideration can be divided into three classes:

Class 1: contaminants typical for former pesticide application

Class 2: contaminants typical for sewage sludge application

Class 3: contaminants typical on military grounds

Table 1 shows the contaminants and applied concentrations.

Table 1: Contaminants and applied concentrations (in mg/kg fresh soil)

Class	contaminant	High concentration	Low concentration
1	Pentachlorophenol	10	1
	Hexachlorobenzene	10	1
2	Dibutylphthalate	10	1
	Bis (2-etylhexyl)phthalate	10	1
	Tergitol NP-9	10	1
	4-Nonylphenol	10	1
3	Trinitrotoluene(TNT)	10	1
	2,6-Dinitrotoluene	10	1
	2,4-Dinitrotoluene	10	1
	2-Nitrotoluene	10	1

The application of the test substances and filling of lysimeters was performed by adding 70 g each of the dissolved substances to 35 kg air dried soil which was previously sieved to 2 mm, homogenisation and dilution by uncontaminated soil to result in the above given concentrations. The contaminated soil material was added to the lysimeters and slightly compressed.

The lysimeters and their adjacent areas were planted by six different crops and vegetables, respectively. Cultivation, fertilisation, pesticide application and harvest were performed according to good agricultural practice. Some of the lysimeters were covered by geotextiles in order to account for contribution of chemicals volatilization from the soil surface and aerial deposition, respectively (e.g. for phthalates).

The experiments were run for the period of one year, where after harvested plants as well as the contaminated soil layers were analysed for the contaminants.

2.3. Sample treatment, clean-up and analyses

Carrots and potatoes were washed, peeled, weighed and cut up small. Haulm (from carrots), pods and further parts were stored at -20°C. Leaves of ryegrass were cut and fro-

Table 2: Clean-up and analyses of soil and plant samples

Contaminant	Soil clean-up	Plant clean-up	Analytical techniques
Pentachlorophenol and hexachlorobenzene	Extraction by 1. acetone / toluene and 2. toluene (acidic), derivatisation by MSTFA	Extraction by dichloromethane (acidic), gelpermation chromatography, derivatisation by MSTFA	GC-MS
Phthalates	Dilution by water, extraction by butylmethyl-ether, concentration, re-solution in hexane and further purification on silica-gel	See soil clean-up	GC-MS
4-nonylphenol and nonylphenol-ethoxylate	Dilution by water, acidification, extraction by cyclohexane, derivatisation by PFBCl	Due to degradability in soil no transfer was observed and thus plant clean-up was obsolete	NCI-GC-MS
Nitroaromatic compounds	Addition of methanol and extraction by sonification, centrifugation, filtration, concentration	Homogenisation under liquid nitrogen, addition of methanol and extraction by sonification, further details on clean-up depending on plants	HPLC

zen. Ears of barley were frozen completely as well as rape seeds. Down-to-earth and upper leaves of curly cale were separated and stored separately.

Prior to the chemical analyses the soil and plant samples were subjected to a clean-up procedure. A brief overview on the procedures as well as the analytical techniques is given in the following table 2.

3. RESULTS AND DISCUSSION OF LYSIMETER EXPERIMENTS

3.1 Stability in Soil

The following table compares literature data on the compounds stability in soil and the results obtained in the lyismeter studies. Disappearance times given as DT50-values or by qualitative description are listed.

Published data confirm the results obtained in the lysimeter studies. In detail it can be discussed for the three classes:

Class 1: contaminants typical for former pesticide application

- **HCB**
  Measured values confirm the known stability of HCB in soils.
- **PCP**
  Half-life times both of published and herein measured studies are in good agreement. Obviously, small laboratory systems enhance degradation in soil. This might by due to a homogeneous mixing and thus distribution of the text substance in the soil system.

Class 2: contaminants typical for sewage sludge application

- **DEHP**
  Published and herein measured data show the degradability of DEHP in active soils. Thus, the compound should not accumulate in soils applied by sewage sludge.
- **NP/NPEO**
  NP and NPEO are easily degraded in soils. The degradation rate is such that a soil-plant transfer should not occur.

Class 3: contaminants typical on military grounds

- **Nitroaromatic compounds**
  Degradability of nitroaromatic compounds depends on their bioavailability. Compounds found at brownfield sites are distributed inhomogeneously, they agglutinate and are not available to microorganisms. Nitroaromatic compounds which are homogeneously distributed in soils – as it is the case for soils under agricultural use – are easily accessible to microorganisms and can be metabolized. Thus, nitroaromatic compounds in agriculturally used soils should be degraded within one years time and thus not taken up by crops and other plants.

It can be concluded that stability and fate in soil is a key element in the evaluation of organic compounds in the context of soil-plant transfer.

Table 3: Literature results for disappearance time DT50 of compounds investigated in the lysimeter study

	Disappearance time DT_{50} [d], literature				Disappearance time DT_{50} [d], this study
compound	BUA–report No. 230	Terytze et al.[1)]	MUNLV[3)]	Swiss study [2)]	
HCB	–	–	–	–	Stable for one year
PCP	10–30d	6,4 ± 2,4d	Not detectable in sewage sludge	–	13 d
DBP	–	–	–	„few days"	< 7 d
DEHP	–	–	"mean" persistence	„fast degradable", DT50 < 30d	64 d
NP	–	4,3 ± 2,4d	–	7,8 h	< 7 d
TNT	–	–	–	–	3,6
2,4–DNT	–	–	–	–	18,0
2,6–DNT	–	–	–	–	21,5
2–NT	–	–	–	–	38,6

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[2]) The Swiss Consortium EPF Lausanne - ENAC – ISTE – CECOTOX / Agroscope FAL Reckenholz refers in the report R. Brändli et al.: Vorkommen und Bedeutung von organischen Schadstoffen in Kompost, Gärgut und organischen Abfällen (Literaturstudie,) to: Chemosphere 35 (4) 667 – 749 (1997)

[3)] Publication of MUNLV: Abfälle aus Kläranlagen in Nordrhein-Westfalen, Teil D: Organische Schadstoffe in Klärschlämmen aus der kommunalen Abwasserbehandlung (2004)

3.2 Soil-plant transfer

The above given summarized results showed sufficient stability of hexachlorobenzene in agriculturally used soils. A soil-plant transfer was measured and transfer coefficients were calculated by forming the quotient of concentration in plants / concentration in soil. Table 4 comprises the results for the crops and vegetables under consideration. Highest concentrations were found in the pods of carrots whereas in corn the concentrations were below the level of determination.

Table 4: Transfer coefficients for HCB

Plant	Transfer coefficient
Carrot (total, not peeled)	0,46
carrot, pod	2,62
potatoes	0,31
Rye gras	0,01
curly cale	0,01
barly, corn	<< 0,01
rape, corn	<< 0,01

4. CALCULATION OF THE MAXIMUM TOLERABLE SOIL CONTENT FOR HEXACHLOROBENZENE

It can be concluded that – due to a sufficient stability in soil and a soil-plant transfer potential – out of the ensemble of tested compounds the calculation of the maximum tolerable soil content is to be performed for HCB only. Following the approach presented in chapter 1.1 the vegetable out of the tested set with the highest transfer coefficient is the basis for further considerations. Thus, the mean transfer coefficient for not peeled carrots (i.e. 0,46) is used. Further information needed is:

maximum residue level = 0,05 mg HCB/kg vegetable [Anonym, 1999d]
water content (carrots) = 88,2% [Anonym, 1999b]
hazard factor = 5,5 [Anonym, 1999c]

It can be calculated:

Maximum tolerable soil content (carrots)
= 5,5 x 0,05 mg/kg / 0,46 [1 – 88,2/100] = **5,1 mg/kg**

Due to the comprehensive data base the application of any safety factors is obsolete.

A comparison of the calculated maximum tolerable soil content with the stipulated trigger value for the path soil-human being (playground) as well as with background values shows table 5.

Table 5: Plausibility check: comparison with trigger and background values

Typcical concentrations for grassland	0,2 – 12 µg/kg
Typical concentrations for agricultural soils	0,5 – 13 µg/kg
Background values in Baden-Württemberg and Hamburg (90. percentile)	1,9 – 10 µg /kg
Trigger value (path soil – human being, playground)	4 mg/kg
Trigger value (path soil – human being, housing area)	8 mg/kg
Calculated maximum tolerable soil content (soil – plant uptake)	5,1 µg/kg

Such a comparison highlights that current HCB concentrations in soils under different uses are lower by a factor of 380 to 25.500 compared to the maximum tolerable soil concentration for the objective „quality of food“.

SUMMARY AND CONCLUSIONS

The procedure to derive soil trigger values for the objective of protection „quality of food and feed“ is conclusive and presents a pragmatic approach. The approach differs in respect to the procedure selected for metals and metal compounds. In case of an insufficient data base safety factors are applied. The suggested factors can be interpreted as „signals“ for further discussions in ad-hoc working groups, and for optimisation or mutually agreed interpretation of the current data set. For organic chemicals the airborne impact, i.e. wet or dry deposition, additionally should be taken into account.

An experimental design which enables the differentiation between exposure pathways and is sufficiently large to exclude disturbances by the experimental equipment is an outdoor lysimeter plant with lysimeters of 1 m^2 surface area.

5 substances and groups of substances, respectively, being evaluated as of high priority, namely HCB, PCP, nonylphenol and –ethoxylates, phthalates and nitroaromatic compounds, were applied to the lysimeters at concentrations of 1 mg/kg soil and 10 mg/kg soil. Lysimeters were planted or seeded with six different crops and vegetables. Treatment, fertilization, pesticide application, and harvest were performed according to good agricultural practice.

Out of the set of tested compounds HCB showed sufficient stability in soil and a soil-plant transfer potential. Thus, the calculation of maximum tolerable soil content was performed using the previously derived concept. A maximum tolerable soil content (on the basis of results for carrots) was calculated as 5,1 mg/kg soil. Due to the comprehensive data base the application of any safety factors was obsolete.

A comparison of the calculated maximum tolerable soil content with the stipulated trigger value for the path soil-human being (playground) as well as with background values shows that current HCB concentrations in soils are lower by a factor of 380 to 25.500 compared to the maximum tolerable soil concentration for the objective „quality of food“.

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PESTICIDE RESIDUES IN THE EGGS OF PEREGRINE FALCONS AND OTHER WILD BIRD SPECIES IN BADEN-WUERTTEMBERG – PRESENT STATE AND TIME TREND

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ABSTRACT

The concentrations of chlorinated pesticides have been measured in eggs of peregrine falcons, owls, jackdaws and tits from the German state of Baden-Wuerttemberg. Data from failed falcon eggs are available for DDT, HCH, hexachlorobenzene (HCB), and heptachloro-epoxide (HCEP) from 1970 to 2003.

During the past 35 years the organochlorine pollution of the eggs of wild birds shows a general decrease which is paralleled by an encouraging increase of the number of breeding pairs of the peregrine falcon in the state. Whereas DDT-concentrations have decreased by a factor of 5 and still exceed 100-fold the limit value for the human consumption of chicken eggs, the 1000-fold decline of the HCB pollution is much more pronounced. In the eggs of the peregrine falcon this compound has reached an average level of 0.05 mg/kg dry matter that in chicken eggs would be considered safe for human consumption. With HCEP and ã-HCH an intermediate decline of the pollution of falcon eggs (by factors of 60 and 300, respectively) has been observed during the past 35 years.

Despite the decline observed, the organochlorine pollution of eggs of the peregrine falcon is still alarming. This assessment is based on the following comparison: Toxic equivalents of 2,3,7,8-tetrachlorodibenzodioxin (contributed by polychlorinated dibenzo-dioxins/-furans and biphenyls) have reached the 'no observed adverse effect level' (NOAEL) in the least polluted eggs of this species, and exceed this level 5-fold in the most polluted ones. The NOAEL was established by Elliott et al. (2001) in osprey chicks, which can be considered similarly sensitive as falcon chicks.

Differences in the distribution pattern among bird species and among organochlorine compounds are shown. Attempts were made to establish factors that influence the regional distribution of DDT and PCB, the two main organochlorine pollutants in eggs of the peregrine falcon.

Health and survival of individual falcons and of the statewide population are still at risk through persistent organic pollutants. Therefore, the monitoring of eggs should continue, and measures to reduce the contamination should be considered where appropriate.

INTRODUCTION

The opportunity to present some results on the analysis of birds' eggs for persistent organic pollutants, especially organochlorine pesticides, is greatly appreciated. The project presented here is part of the bio-monitoring program of the German state of Baden-Württemberg (B-W). B-W is one of the states of the Federal Republic of Germany, located in the southwest, with a population of ca. 10 million (Figure 1).

Figure 1: The German State of Baden-Wuerttemberg

The bio-monitoring program of the state comprises the measurement of effects or pollutant concentrations at forest-, river-, and grassland-observation plots, the monitoring station at the river Rhine, where continuous bio-monitoring with Daphnia magna and fish is conducted, and temporary measuring sites, e.g. at the motorway (fig. 2). The

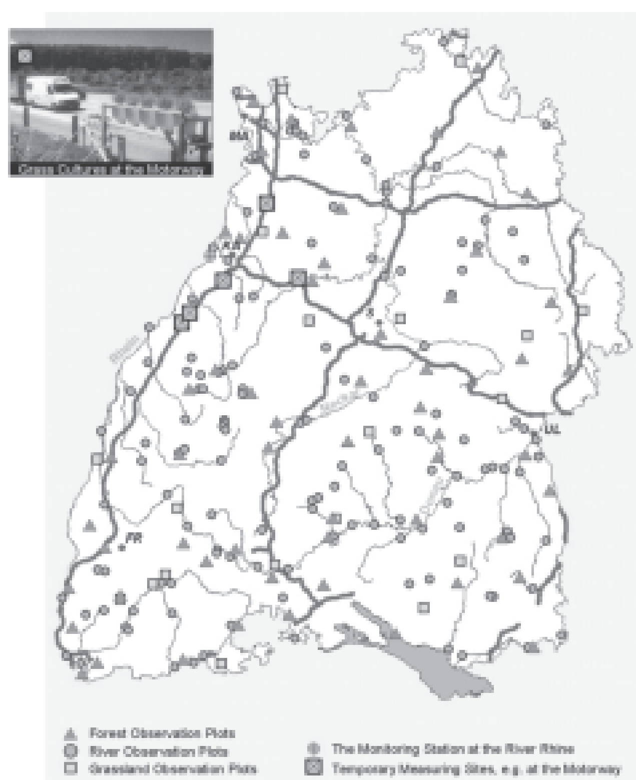

Figure 2: B-W's ecological effect survey program

program is carried out by the State Environmental Protection Agency (Landesanstalt für Umweltschutz Baden-Württemberg – LfU).

Part of the program is aimed at measuring pollutants in biological materials. Pollutants are chemical substances released inadvertently in the course of the advancement of technology. These substances may have dangerous effects on humans, animals, plants, or ecosystems. They may be toxic, mutagenic, carcinogenic, or disrupt reproductive or endocrine functions. But also their mere persistence in the environment and accumulation in biota may cause concern. Therefore it is necessary to continuously monitor and control these substances.

Most pollutants are synthetic products that do not naturally occur in the environment. Organochlorine (OC) pesticides have been used as insecticides and fungicides in agriculture and forestry as well as in veterinary and human medicine. Some examples are dichlorodiphenyl-trichloroethane (DDT), hexachlorobenzene (HCB), heptachloroepoxide (HCEP), and hexachlorocyclohexane (HCH).

Polychlorinated biphenyls (PCBs) are industrial chemicals. They have been used as insulating materials in electrical equipment such as capacitors and transformers, as plasticizers in waxes, in paper manufacturing, and as heat exchange as well as hydraulic fluids. Moreover they have been added to products such as flame retardants, sealants, and lacquers. Polychlorinated dibenzodioxins and –furans (PCDD/Fs) have never been produced on purpose, but arise from the combustion of organic materials in the presence of chlorine. HCB that has been used as fungicide and seed dressing, also originates as unintentional by-product in fires.

Due to their physical/chemical properties, these persistent organic pollutants (POPs) are distributed and accumulated in different compartments of the environment. Their solubility in water is generally low with a corresponding high lipid solubility and resistance to degradation. In spite of the low vapour pressure, these properties are responsible for the evaporation from an aqueous solution and the subsequent long range atmospheric transport and global distribution of these substances. Consequently, one can observe their ubiquitous occurrence with a marked bioaccumulation especially in lipophilic compartments (Wania, 2004).

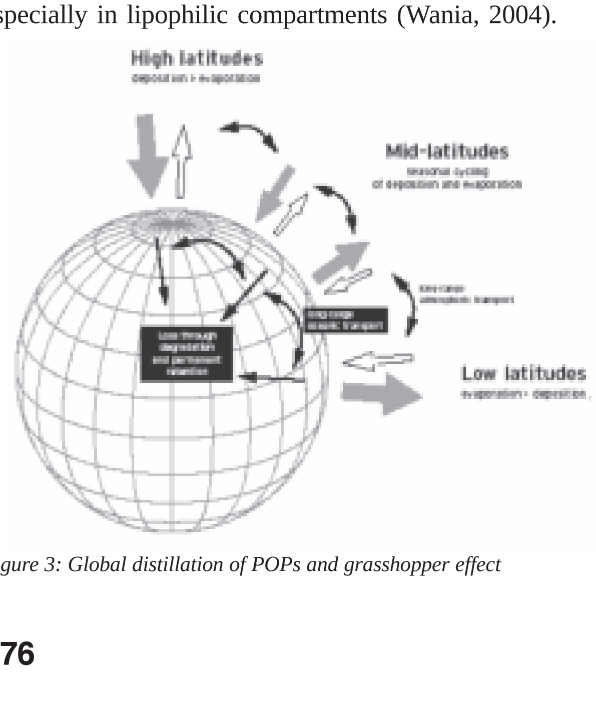

Figure 3: Global distillation of POPs and grasshopper effect

Due to climatic differences, persistent chemicals tend to evaporate from low geographical latitudes and freeze out at high latitudes and high elevation. This effect is called cold condensation or global distillation (Figure 3).

The grasshopper effect of consecutive evaporation and deposition applies to chemicals which undergo particle-bound transport, because their volatility is too low for gas phase transport.

Meanwhile the production and application of these POPs have been banned in Germany because of their dangerous properties for the environment. Nevertheless, they are ubiquitous in the environment because of their earlier use. We, therefore, determined for Baden-Wuerttemberg the concentrations of these substances in suitable bio-indicators and possible effects in living organisms.

METHODS

Birds' eggs were used for the bio-monitoring of these substances as they are relatively accessible and can accumulate lipophilic pollutants because of their lipid content. We collected eggs (or embryos of different stages) from peregrine falcons, owls, jackdaws, and tits for the investigation.

Nest boxes were hung up at selected sites by the LfU to collect the first clutch from titmice. The eggs of the other species were collected by private organizations for the protection of birds [such as the Forschungsgemeinschaft zur Erhaltung einheimischer Eulen e.V. (FOGE; Research Community for the Conservation of Indigenous Owls) and the Arbeitsgemeinschaft Wanderfalkenschutz (AGW; Working Community for the Protection of peregrine Falcons)].

These organizations regularly ring the juveniles and remove failed eggs for the analysis. The samples were analyzed partly by the Chemisches und Veterinäruntersuchungsamt (CVUA; Chemical and Veterinary Investigating Office) Freiburg and partly by a commercial chemical laboratory.

RESULTS AND DISCUSSION

Figure 4 displays the results of the analyses of 2001. The concentrations of PCBs and the OC pesticides DDT, HCB, dieldrin, HCEP, beta- and gamma-HCH, and chlordane in the eggs of different bird species are shown.

Concentrations differ by four powers of 10 between different substances and different bird species. For different

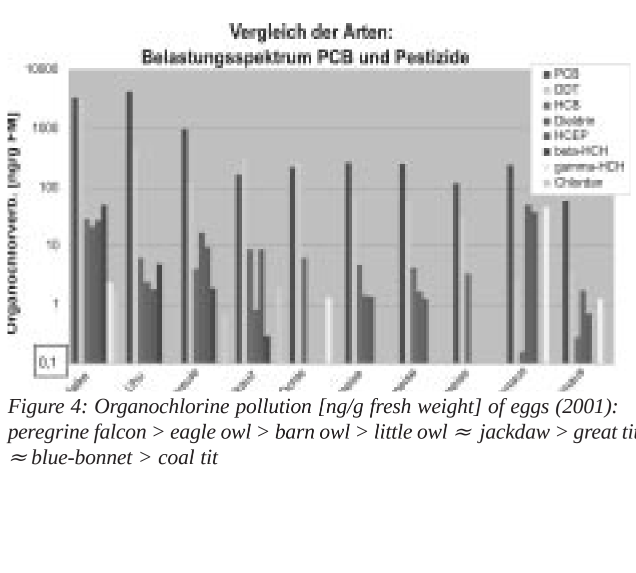

Figure 4: Organochlorine pollution [ng/g fresh weight] of eggs (2001): peregrine falcon > eagle owl > barn owl > little owl ≈ jackdaw > great tit ≈ blue-bonnet > coal tit

species the position in the food chain can be concluded. The total OC pollution of the eggs decreases in the order of:

peregrine Falcon > Eagle Owl > Barn Owl > Little Owl ≈ Jackdaw > Great Tit ≈ Blue-Bonnet > Coal Tit.

The peregrine falcon (Falco peregrinus) is the most highly polluted bird species within the project (Figure 5). This beautiful predator was on the brink of extinction around 1970 because of the egg-shell thinning caused by DDT. Less than 30 breeding pairs were left in Baden-Württemberg, and from most other German states the bird had disappeared. Today around 300 pairs are breeding in the state of B-W.

Figure 5: The peregrine falcon is the most highly polluted bird species within the project (Photo: B. Zoller)

The analysis and evaluation of the organochlorine pollution for 35 years permitted the establishment of long-term trends. These investigations were initiated by the private working community of falcon protectors (AGW) in collaboration with the Chemical and Veterinary Investigation Office Freiburg (CVUA-FR) as early as 1967. Through the collaboration with the initiators of the project the LfU can now present valuable time series of the pollution of eggs of the peregrine falcon by various organochlorine compounds (DDT, HCB, HCEP, lindane, and PCBs, Figures 6 - 10). All of these show an encouraging decrease in the 1970s, PCBs in the 1980s.

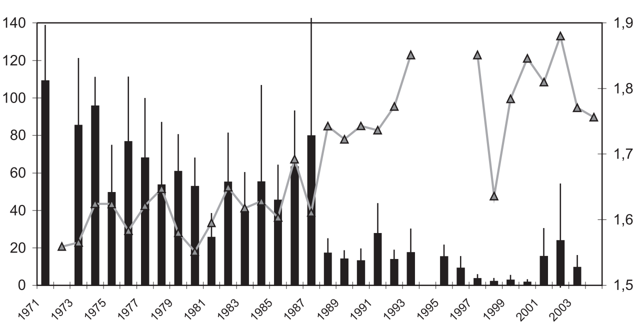

Figure 6: Time trend of DDE [µg/g dry matter with standard deviation], left scale, in eggs of peregrine falcons from Baden-Wuerttemberg. The egg shell index (Δ right scale) is related to shell thickness

In the case of DDT there is no question that the ban has contributed significantly to prevent the extinction of the peregrine falcon. The critical threshold for the extinction of a population is 75 – 100 µg total DDT/g dry matter (= 250 – 330 µg/g lipid; Schilling & Wegner, 2001; Wegner et al., 2005). DDT and its most important metabolite DDE (dichlorodiphenyl-dichloro-ethane) disturb the calcium-metabolism in birds and lead to egg-shell-thinning which ultimately jeopardizes the hatching success and the reproduction. More than 99% of the total DDT in the eggs of the peregrine falcon is contributed by the more persistent DDE. Therefore, only DDE was plotted over time. The actual level of 10 - 20 µg/g (dry matter) may seem low compared with the contamination of the early 1970s of more than 100 µg/g (Figure 6). But the present DDE-contamination of the eggs of the peregrine falcon exceeds the limit value for the feed of livestock (0.1 µg/g dry matter) by a factor of 100 – 200.

HCB was used as seed dressing. In 1973 the concentration of this substance in peregrine eggs exceeded the limit for food products 1000-fold (Figure 7).

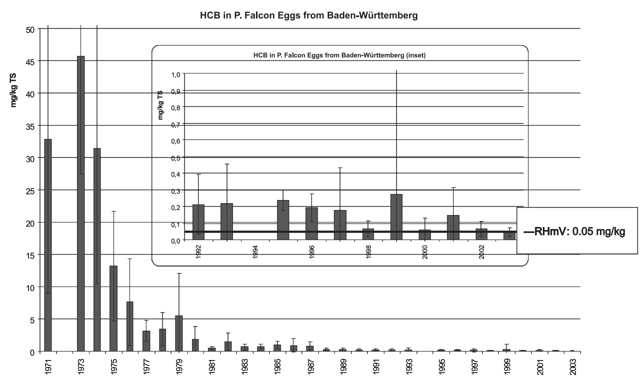

Figure 7: Hexachlorobenzene (HCB) in peregrine eggs – time trend

In 2003 this limit was met for the first time in 20 years. The average level of 0.05 µg/g dry matter would be considered safe for human consumption in chicken eggs because of the EU limit of 0.2 µg/g lipid according to Council Directive 86/363/EEC which corresponds to 0.05 µg/g dry matter. This pollution decline by a factor of 1000 is an impressive demonstration of how successful banning a substance can be.

A similar decline by a factor of 300 was observed with lindane (gamma-HCH, Figure 8). HCH concentrations clearly exceeded the limit value in the early 1980s. They are now below the detection limit.

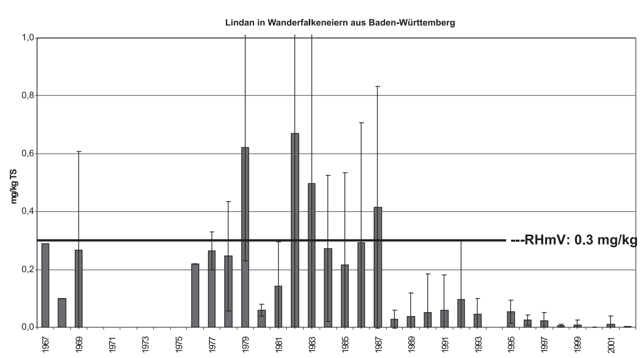

Figure 8: Lindane (gamma-HCH) in peregrine eggs – time trend

HCEP decreased by a factor of 60 (Figure 9). This decline, however, is not sufficient to meet the requirement of the limit value, which is still exceeded twofold.

The PCBs peaked towards the end of the 1980s with 140 µg/g dry matter and receded to 40 µg/g in the 1990s and 20 µg/g after 2000 (Figure 10). PCBs are thought to indicate densely populated and highly industrialized areas. Despite

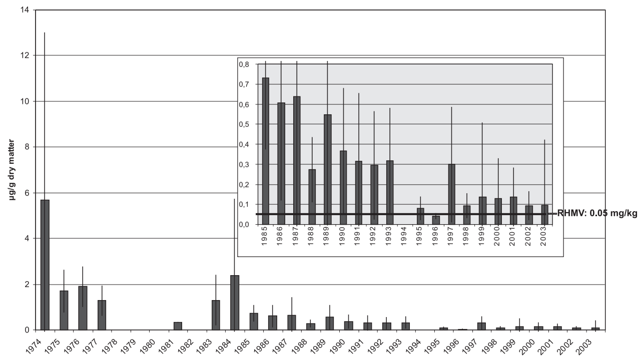

Figure 9: Heptachloro epoxide (HCEP) in peregrine eggs – time trend

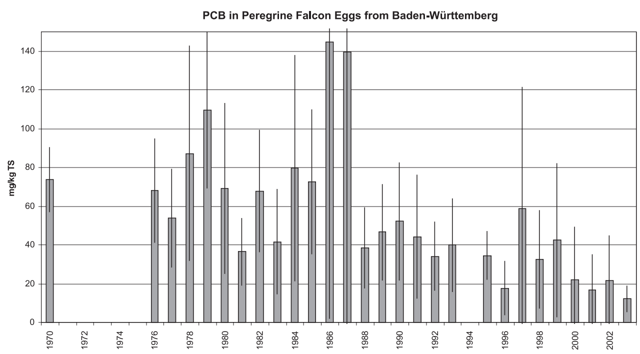

Figure 10: Total PCBs in peregrine eggs – time trend

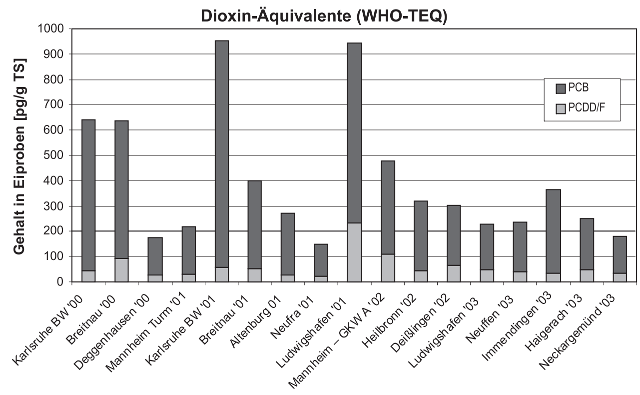

Figure 11: Dioxin equivalents [pg/g dry matter] in selected peregrine eggs from four years

the ban, they are still released from house-building materials and electrical appliances. These local sources may be the reason why their decline is not more pronounced. Even now they exceed the limit value 5fold (SHmV, 2003: ca. 3 µg/g dry matter = 0.6 µg/g wet weight; 0.02 µg/g wet weight for each of six congeners whose sum is multiplied times five according to DIN).

The co-planar PCBs act bio-chemically like dioxins. Toxic equivalence factors (TEFs released by the WHO, 1998) for the dioxin-like potency of 4 non-ortho-PCBs and 8 mono-ortho-PCBs were applied to evaluate the falcon egg data for dioxin toxic equivalents (WHO-TEQ).

Because of the high cost of dioxin analysis only 17 eggs could be analysed for PCDD/F in the years between 2000 and 2003. The total pollution with dioxin equivalents (WHO-TEQ) was calculated for these eggs and is plotted in Figure 11. Dioxins and furans contributed only 15% of the TEQ, whereas 85% may be attributed to the PCBs. The contamination peaked at above 900 pg/g (dry matter), and these values exceed the EU limit value by a factor of more than 1000. This limit value (of 0.75 pg/g dry matter ? 3 pg/g lipid; EG, 2001) was derived for chicken eggs for human consumption and includes a safety factor. Humans are not at risk through falcon eggs. But the falcon embryos most likely are. For birds of prey a risk level of 200 pg/g was determined in osprey chicks (NOAEL = red line in Figure 11; Elliott et al., 2001). A similar sensitivity of ospreys and peregrines may be presumed, and no safety factor is included. All the eggs measured are contaminated up to this threshold of dioxin action and some exceed it significantly by up to a factor 5. Despite the decline in OC concentrations in the past decades the peregrine population of Baden-Württemberg is still at risk through OC compounds in their environment. These compounds may stem predominantly from local sources like the PCBs or from long range transport like the pesticides.

The DDE concentration in falcon eggs (Figure 6) displays a rise in recent years (2001 – 2003). The source of this recent contamination is unclear; a likely explanation is long range transport from countries still applying DDT. A combined action of DDE and PCB is possible because of the similar chemical structure. The dioxin-like potency of DDT has not been determined so far. For a complete assessment of adverse effects of organohalogen compounds it is necessary to know the toxic potency of compounds such as DDT, DDE, and the polybrominated diphenyl ethers (PBDEs), which were determined in concentrations about 100fold lower than PCBs in falcon eggs of 2003.

The approach of Schröder & Schmidt (2001) was used to divide the state into 20 eco-regions according to soil properties, vegetation, climate and elevation. In six of these eco-regions a sufficient number of falcon eggs could be analyzed in 2001 -2003 to calculate a meaningful regional average pollution. The mean concentration in falcon eggs of the main pollutants in these eco-regions is shown in Figure 12.

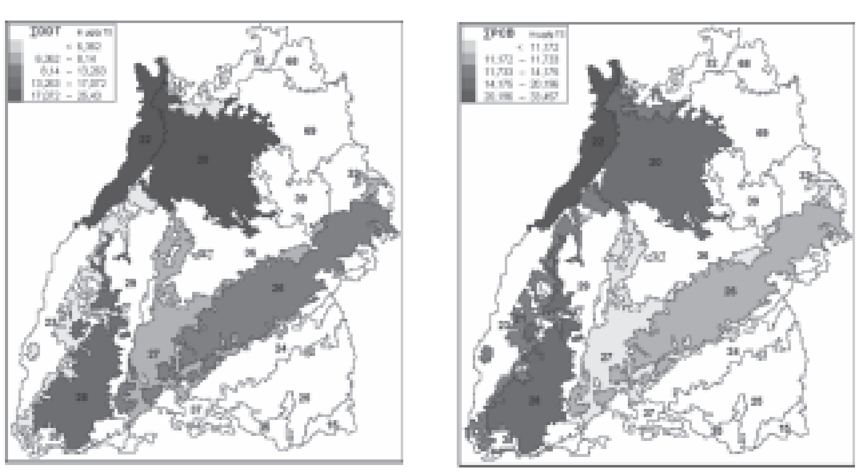

Figure 12: Average organochlorine pollution of peregrine eggs from six eco-regions (2001 – 2003)

The following conclusions can be drawn from this regional analysis:

1. The most highly polluted areas in

the northwest are densely populated and industrialized. This applies to both DDT and PCB.

2. The two highest mountain ranges (Black Forest and Alb) are remote from industry and urban centres, but still polluted. The peaks of the Black Forest extend into an arctic climate zone.

3. The lower areas immediately west (= windward) of these mountains are less polluted than the high regions by one or two classes. This confirms within the state of Baden-Wuerttemberg the global distillation theory of long range transport and cold condensation of these compounds (Figure 3).

CONCLUDING REMARKS ON LONG TERM EFFECTS OF DDT REPRESENTING OBSOLETE PESTICIDES

DDT was first synthesized in Germany in 1874. After a latency period of 65 years its insecticidal activity was discovered by Paul Müller in 1939, who received the Nobel Prize for his discovery. Thirty three years later in 1972 the population of peregrine falcons had become extinct in most German states through the application of DDT, and the substance was banned in Western Germany. And another 33 years later in 2005 we are still troubled by the very same compound which is being carried back by the wind from remote continents to which we first exported it.

When will the DDT-problem be solved?

The authors hope that this conference will contribute to solving the problem of obsolete pesticides, and thank all those cooperating to this end.

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TOXICITY OF PESTICIDES IN THE PRESENCE OF HEAVY METALS ON BIOCHEMICAL OXIDATION OF AMMONIA IONS

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Toxicity is a general term used to indicate adverse effects produced by pesticides.

Four types of toxicity are known, types based on the amount of exposure to a pesticide and the time it takes for toxic symptoms to develop. At one end of the scale is the type that is caused by short-term exposure and happens within a relatively short period of time, and at the other end of the scale you find long-term exposure that happens over a longer period of time.

Various ways of measuring toxicity have been developed to measure this properly, including the mean lethal dose or LD50. However, it must be said that the value from LD50 should be interpreted cautiously since there is a wide difference in response between different species of organic life.

The dosage of pesticide determines, to a large extent, the outcome of poisoning caused by them. It is important to note that a sufficiently large dose of an ordinarily harmless material is fatal. On the other hand, a sufficiently small dosage of the most toxic pesticide is without effect.

The toxic manifestations of a pesticide may vary depending not only on the dose but also on the duration of the exposure. For many pesticides, the toxic effects observed from a single exposure may be quite different from that of repeated exposure.

Some pesticides may cause irreversible or permanent damage. They can effects one toxicity and in presence of different compounds - other toxicity.

As in any other country, the river network in the Republic of Moldova is the final receptor of most runoff and wastewater, either household or industrial. The treatment level of wastewaters is insufficient and 1/3 of pollutants, including pesticides and some heavy metals, still persist after treatment, which is discharged into natural waters. The concentrations of other pollutants, such as ammonia ions, regularly exceed the MACs.

The content of analyzed metals in the Dniester river: Mn - 3.2-32.6 μg/dm^3, Pb – 1.8-3.7 μg/dm^3, Al – 12.8-42.1 μg/dm^3, Ti – 1.1-3.5 μg/dm^3, Mo - 1.7-2.8 μg/dm^3, Ni - 2.4-4.2 μg/dm^3, V - 1.6-2.7 μg/dm^3, *Cu -1.9-18.9 μg/dm^3, Zn - 18.8-178 μg/dm^3*, Cd - 0.9-4.1μg/dm^3, Cr - 0.3-1.7 μg/dm^3. The highest concentrations are recorded downstream of the confluence with river Bac (carrying the wastewater from the capital city

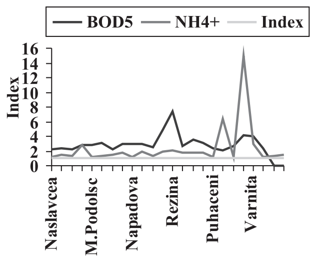

Figure 1: Spatial evolution of the Dniester water quality

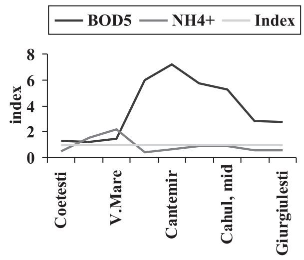

Figure 2: Spatial evolution of the Prut water quality

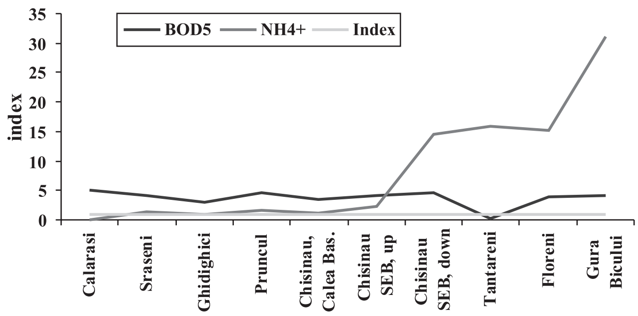

Figure 3: Spatial evolution of the Bic river water quality

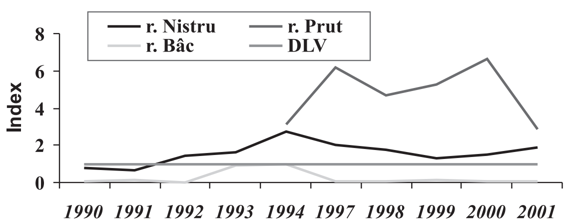

Figure 4: Discharge of ammonium into the surface waters

Chisinau) and upstream the cities of Soroca, Tighina and Tiraspol: zinc (122 - 176 µg/dm^3) copper (26,8 µg/dm^3 – 32 µg/ dm^3), nickel (17,8 µg/dm^3 - 19,1 µg/dm^3) and so on.

The poor water quality in small internal rivers is an issue of permanent concern. The concentrations of ammonium, nitrites, phenols and copper regularly exceed the MACs. The Index (water pollution index - ratio of the substance discharged and the discharge limit value) for different rivers is given in Figures 1-3. Ammonium concentrations of 17.0 mg/dm^3 as N (43.6 MAC) up to 46.5 mg/dm^3 as N (119 MAC) were found in the Bic river, downstream Chisinau, maintaining their high values up to the confluence with the Dniester river (Figure 4).

Considering that biochemical nitrification is an important process of natural water self-purification and that wastewater treatment plants and many pollutants influence it, the aim of this work was to investigate the role of some pesticides (lindane - L and dieldrin - D) and heavy metals (Cu and Zn) in mentioned process.

In view of the fact that the change of microorganisms content in function of the speed does not have a linear character, an analytical solution to the problem was realized by control of NH_4^+, NO_2^-, NO_3^-, O_2 and pH.

Water samples for modeling were collected from river Nistru. Initial concentration of ammonia ions was created by adding 2 mg/dm^3 of NH_4^+ ions, 1 – 5 MACs of lindane, dieldrin, Cu and Zn.

From the obtained analytical results it was established that the transforming $NH_4^+ \rightarrow NO_2^-$ process (Table 1) is totally inhibited in 15 – 20 days (analogically to control) in the presence of CuZnLD mixture (1 maximal admissible concentration - MAC), ZnLD ones (2 MAC).

The activity of microorganisms in $NO_2^- \rightarrow NO_3^-$ transformation (table 2) is influenced by CuZn (1 MAC), Cu, L, ZnLD (2 MAC).

So the toxic manifestations of the pesticides on biochemical oxidation of ammonia ions may vary, depending not only on the dose but also on the nature of other pollutants in the water system.

Table 1: The dynamics of NH_4^+ (%) remained in modeling system ($NH_4^+ \rightarrow NO_2^-$)

Conditions of model	Days											
	0	2	4	6	8	10	15	20	25	30	35	40
CuZnLD (1 MAC)	100	92	86	76	69	67	61	55	51	43	40	40
Cu (1 MAC)	100	96	88	86	79	61	51	25	0	0	0	0
CuZn (1 MAC)	100	96	90	86	77	63	47	21	0	0	0	0
Zn LD (2 MACs)	100	98	91	85	71	61	45	20	0	0	0	0
ZnD (5 MACs)	100	97	93	88	72	64	48	20	0	0	0	0
Zn (5 MACs)	100	97	90	84	72	63	47	18	0	0	0	0
L (2 MACs)	100	96	73	47	0	0	0	0	0	0	0	0
D (5 MACs)	100	95	75	47	0	0	0	0	0	0	0	0
Control	100	88	72	31	0	0	0	0	0	0	0	0

Table 2: The dynamics of nitrites (mg/dm^3) generated in $NO_2^- \rightarrow NO_3^-$ process

Conditions of model	Days									
	0	2	4	6	8	10	15	20	25	30
CuZnLD (1 MAC)	0	0	0,12	1,18	2,6	3,6	4,2	2,4	0,5	0
Cu (1 MAC)	0,02	0,08	1,5	3,8	4,6	5,5	2,0	0,2	0	0
CuZn (1 MAC)	0	0	0	0,07	0,09	0,02	0	0	0	0
Zn LD (2 MACs)	0	0	0,04	0,07	0,03	0,01	0	0	0	0
ZnD (5 MACs)	0	0	0,07	0,15	0,18	0,03	0	0	0	0
Zn (5 MACs)	0	0	0,02	0,11	0,08	0	0	0	0	0
L (2 MACs)	0,02	0,25	3,2	5,1	4,9	1,7	0	0	0	0
D (5 MACs)	0,015	0,11	0,66	4,3	2,3	1,6	0	0	0	0
Control	0,03	0,55	2,70	5,60	1,30	0,67	0,5	0,2	0,05	0

It is important to take into account the content of heavy metals and pesticides in wastewater treatment plants' activity.

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ELIMINATION OF ACUTE RISKS OF OBSOLETE PESTICIDES IN MOLDOVA, ARMENIA AND GEORGIA

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1. INTRODUCTION

Pesticides manufactured for agricultural and/or health purposes that have become redundant and unfit for use are defined as "Obsolete pesticides" (Vijgen, 2005). Reasons that pesticides have become obsolete can be that the products are banned by legislation, physically unsuitable to be used due to deterioration or otherwise, decrease of active components compared to the manufacturers' specifications.

At present the following pesticides: hexachlorocyclobenzene (HCB), DDT, Dieldrin, Endrin, Aldrin, Heptachlor, Toxaphene, Chlordane, and Mirex are classified as persistent organic pollutants (POPs) and they are forbidden to be used (under Stockholm Convention). (www.pops.int).

The problems on obsolete pesticides are complex and can not be solved within a time span of a few years. Proper storing and repackaging can reduce the risks regarding the obsolete pesticides and incineration of the pesticides can lead to the final removal of the direct risks of pesticides. A permanent solution for the removal of the pesticide substance should however not ignore the risks of abandoned and old storage sites where obsolete pesticides were stored. The improper storage of pesticides can lead to negative effects of the soil and surrounding due to their highly toxic and persistent character. They also evaporate and travel long distances through air and water and accumulate in fatty tissues (www.pops.int).

The project "Elimination of Acute Risks of Obsolete Pesticides in Moldova, Armenia and Georgia" (2005-2007) focuses on activities concerning the elimination of acute risks of obsolete pesticides. The project being implemented in phases have started in Moldova and Georgia. Interim results and developments are being described in this article.

2. CURRENT SITUATION IN EASTERN EUROPE

2.1 Introduction

During the sixties of the previous century the use of pesticides in communist countries was thought to enable the increase of agricultural production to match with the West. This led to a gigantic over-production and over-use of pesticides as the products were distributed freely to the farmers. After the collapse of communist system, many storages of pesticides and stocks unfit for use were not maintained or taken care of properly. Privatisation re-introduced private ownership and farmers got their land back; ownership for pesticides storages however reduced. Eastern Europe, Caucasus and Central Asia (so-called EECCA region) now are facing the presence of hundred thousands of tons without an owner.

Looking at the current situation, it is known for instance that Ukraine has at present about 5000 locations, which contain obsolete pesticides.

2.2 Situation in Moldova

The Moldovan government has ratified the Stockholm Convention on POPs. This convention can be a useful instrument to implement future solutions in order to solve the worldwide problems on obsolete pesticides? Convention countries accept the moral obligation to take action. In May 2001 the convention was signed in Stockholm by 150 nations; the convention has entered into force in May 2004, when35 countries had ratified. At present already more than 100 countries have ratified the convention.

In addition, the Republic of Moldova ratified the Aarhus Convention on Access to Information, Public Participation in Decision-Making and Access to Justice in Environmental Matters in 1999.

Moldovan authorities are strongly committed to solve the problems with obsolete pesticides. Steps have been taken to support POPs related activities and to provide financial support. The Ministry of Defense (MoD) and the State Department for Civil Protection and Emergency Situations (DES) have begun to repackage and safely store obsolete pesticides. More than 1700 tons of these substances coming from 7 administrative territories called "rayons", out of a total of 37, have been repackaged and stored. In another 14 rayons the National Army together with DES have initiated repackaging.

In 2005 the World Bank prepared the GEF Sustainable Persistent Organic Pollutants (POPs) Stockpiles Management project in Moldova (2006-2009). Main objective of the project is to protect the environment and human health through the sustainable management of POPs pesticides' and PCBs stockpiles. The project aims at environmentally safe disposal and management of POPs by creating national capacities for the implementation of the Stockholm Convention on POPs requirements, and of those stipulated under other relevant international conventions and protocols ratified by Moldova.

2.3 Situation in Georgia

Under auspiciens of the Ministry of Environment several activities were developed and implemented. They developed close cooperation with the Dutch Ministry of Environment. With their help the environmental inspection in Georgia has been established.

The government of Georgia signed but did not ratify the Stockholm Convention on POPs, yet. The Basel Convention on transport of hazardous waste was ratified as was the Aarhus Convention April 11th 2000. Both can be valuable tools in creating a legal base for this kind of work.

The POPs team functioning under of the ministry of Environment has prepared an inventory on obsolete pesticides at national level. In the framework of the UNDP POPs Project information was gathered concerning the reality on obsolete pesticides in Georgia.

With reference to the work executed by the POPs (Persistent Organic Pollutant) project of the Ministry of Environment Protection and Natural Resources of Georgia, so far in Georgia some 46 different sites have been identified containing obsolete pesticides. Reportedly, the preliminary inventory of these sites shows an estimated total amount of suspected hazardous obsolete pesticides of about 357.000 tons for solid and liquid obsolete pesticides respectively. Besides these 46 sites, one central storage site exists containing reportedly 2.800 tons of obsolete pesticides. All sites were visited by regional representative groups and project experts.

3. THE PROJECT

3.1 Objectives and goals

The overall objective of the project is to eliminate the risks of dissemination of obsolete pesticides and to contribute to the improvement of the environment regarding the risks of the presence of pesticides. For each country specific aims have been identified.

The goals set for Moldova are to eliminate the acute risks of dissemination of obsolete pesticides through proper storage and export and destruction of chemicals, and to set an example for the international community, more specifically in Eastern Europe.

Specific project objectives formulated are the transfer of know-how and expertise to local people on taking stock and repackaging of obsolete pesticides, the remediation activities of old storage sites, the repackaging of obsolete pesticides according FAO standards, and, to provide after care and remediation of old pesticide storages. (FAO has a special programme on "Prevention and Disposal of Obsolete Pesticides" (see http://www.fao.org/ag/AGP/AGPP/Pesticid/Disposal/).

The project generally aims at proper storage of obsolete pesticides for a period of maximum duration of 20 years. The project does not directly include measures for transportation of pesticides outside the country during the period 2005-2007. It is important to set realistic goals and set right expectations amongst all stakeholders in order to build up a solid base for cooperation. Nevertheless, it needs to be addressed that the storage is not meant to be permanent, but temporary.

The storage duration is a point that needs to re-discussed and reconfirmed by the different authorities according to the needs and demands of the national situation. In Moldova for instance, it has been agreed to provide storage for much shorter duration, since the activities can be linked with the projects of the Worldbank and NATO. This means that the pesticides repackaged can be removed in a much earlier stage.

3.2 Approach

The problems regarding obsolete pesticides are complex and manifold. A multi-stakeholder approach is being applied in order to address the different aspects regarding obsolete pesticides problem. This enables key players to study and choose options and methods that can tackle the problems. The project activities therefore include follow-up activities regarding the after care of the emptied and abandoned storage sites and surrounding. It also includes measures and opportunities to address questions such as alternatives for use of pesticides in agriculture. .

The project applies a participatory approach involving all stakeholders, groups in society that can play a role in the project. The project therefore involves various target groups such as stakeholders at local and national level as well as the international community including authorities, local public, NGOs, entrepreneurs, farmers, customs et. In addition, international organisations, NGOs and institutions which are involved in dealing with eliminating risks of obsolete pesticides have their role.

Milieukontakt works in cooperation with stakeholders according to the following principles: bottom-up approach, involvement of all stakeholders, participation of civil society groups, creating ownership on local level, focus on process but with tangible results, explore new ways of working, tailor-made approach, and developing cooperation and networking at national and international level.

It is important that all relevant stakeholders can participate in the process, also at the level of decision making and the level of implementation. Stakeholders need to find solutions that can be sustainable for the region and create an ownership of the solutions as well as of the problems regarding obsolete pesticides. The project aims to function as a pilot project to create new valuable experiences, know-how and expertise that can serve as an example for the governmental and non-governmental sector in other regions and countries on how to deal in an effective way with obsolete pesticides.

Milieukontakt believes that the obsolete pesticides need to be managed in an environmentally sound way. Regarding final disposal different alternatives are considered: "no action"; remove to a dump site; destruction in Moldova; and destruction in a western country; proper storage with long term duration. The options should be taken into consideration during the project. Further the remediation and after-care of sites will be addressed as an important part of the overall project.

3.3 Cooperation and partnership

Milieukontakt is a Netherlands support organization, whose main objective is to strengthen environmental movement and democratic developments in civil society. Milieukontakt has an extensive network of organizations and contacts in Central and Eastern Europe through the development and implementation of organizational and institutional capacity building training programmes. Milieukontakt supports environmental campaigns focusing on strategy development, promotes public participation and cooperation between NGOs and authorities.

The project is carried out in close cooperation with the partners TAUW consultancy and International HCH & Pesticides Association (IHPA) and Dutch organisation Stichting Natuur en Milieu. TAUW provides expertise for the training and support on analysis, repackaging and storing of pesticides. IHPA is an independent and non-political network that addresses the world-wide problems stemming from the production and use of HCH and other obsolete pesticides and its dangers for human health and the environment. All activities related to the storing, packing and transportation of pesticides are done according to the international standards of FAO.

The project in Moldova includes governmental and non-governmental partners at various levels. Milieukontakt has developed cooperation with the Moldovan government including the Ministry of Environment and Ministry of Agriculture. The Moldovan government has welcomed the initiative to carry out the project in one of the rayons. Milieukontakt developed close cooperation with governmental bodies such as the Ministry of Defense, Ministry of Environment and the POPs team. After discussions NATO and Ministry of Defense lately expressed their interest and their commitment to the project in the rayon Hincesti. Other partnerships have been developed with the rayon authorities in Hincesti.

For the project implementation in Georgia close collaboration has been developed with the ministry of Environment and the NGO community.

3.4 Activities

3.4.1 Activities in Moldova

Several activities in Moldova have been set up and started last year at local, national and international level.

* Local project in the rayon Hincesti

Through a tender procedure the rayon Hincesti was identified. After a stakeholders analysis the first meeting was held to launch the plans for the rayon. In August the working group of Hincesti was set up consisting of stakeholders from various backgrounds, such as agronomists, agriculture, chemistry, local governmental organisations, NGOs and experts on pesticides and health.

Tasks of the working group are to advise on regional aspects of the project, to make a quantitative and qualitative report on the packaging and destruction of obsolete pesticides and to promote the activities at regional level, to communicate with the public and groups and authorities.

The working group has been quite succesful already after five month of work, publishing leaflets and organising discussion meetings with the public.

The first Local platform meeting October 2005 enabled the working group to create a dialogue between civil society, NGO, local and rayon authorities to discuss the problem of obsolete pesticides in their rayon. They presented the interim results of the analysis and discussed the place for a new central storage in the rayon.

In December the working group organised in cooperation with authorities a public hearing in order to consult the public on the allocation of the site for the central storage. This public hearing was a great success because the working group managed to present well-organised their analysis and proposals to the public and other stakeholders. The discussions during the public hearing were now and then quite emotional but the working group did a great job in explaining the people that the rayon needed the best solution.

After this public hearing the place for a central storage was chosen. The central storage will be in Stolniceni Village. The site was selected because the storage is located away from environmental hazards and relatively safely away from water sources and from human settlements (about 1500 m). Though the storage is near to livestock and crop production the Hincesti Environmental Agency promised to plant a green wall around the storage in spring and autumn 2006 in order to reduce hazards. The storage can easily be reached by trucks during all seasons, because of good access road except for during periods with snow.

Rayon authorities accepted the condition that the rayon budget would provide financial resources for maintenance of the central storage during period of stocking obsolete pesticides. The other condition was also met: the Ministry of Environment guaranteed that the stock in Stolnicen will be exported from Moldova and disposal out of country with the financial support of World Bank project on POPs by August 2006.

In short time the working group has succeeded to form new partnership relations with local municipality and rayon authority in solving problem of OP. They gained recognition as important structure which includes main official bodies working on obsolete pesticides.

* Training and support

The working group and the local inventory team participated in two training courses on obsolete pesticides organised for the rayon Hincesti. The aims of the training courses were to prepare the participants for and carry out the inventory of obsolete pesticides in the rayon. After the second training participants made the inventory of all sites with obsolete pesticides with guidance from the expert on obsolete pesticides. The results of the inventory were presented at the platform meeting. Through the inventory data regarding types of pesticide, type of package material, status of storing, risks, and quantity were registered. In total 60,000 kg of pesticides were identified in Hincesti and 15 people were trained. The working group made an analysis of potential risks and costs of clean up and storing activities and identifying a potential site for central storage.

The working group received training support on organisational capacity and self-organisation in order to become more effectively in meetings with the public and authorities.

* Network development at national level

Stakeholders discussed the current developments and projects regarding obsolete pesticides during a workshop at the fifth Forum of environmental NGOs. Participants included people from government, non-profit sectors, experts and other stakeholders. The greatest achievement of the forum was that NGOs realized that there is indeed a big problem regarding obsolete pesticides and that it is necessary to join efforts. The NGOs community realized that there is a need to continue to study different ways of public participation in environmental matters and that NGOs have to take up their responsibility.

As a follow-up on this national NGO meeting, a working group was formed during the introduction seminar December 2006. The mission of working group is to evaluate and to reduce the impact of pesticides on environment and human health in the Republic of Moldova .Currently they have started to collect best examples on sustainable agriculture to avoiding the creation of new obsolete pesticides and studying possibility for the remediation of sites in Moldova after collecting obsolete pesticides.

The network of stakeholders is being supported through information exchange and knowledge sharing by means of information and communication technologies (ICT). Working groups are supported by means of ICT tools like mailing lists. Data base and online content sharing are in the process of development.

Website space is being created on www.vox.md and in process of elaboration. It will provide space for several initiatives within the framework of the project.

* Advocacy and international cooperation

At international level the project was promoted at the 8th International HCH conference on obsolete pesticides held in Bulgaria May 2005. Awareness was raised to increase public participation in the discussions on obsolete pesticides in Eastern European countries and the need was expressed to strengthen the cooperation among NGOs in Eastern Europe. Milieukontakt wants to stimulate this process in cooperation with the international HCH and Pesticides Association.

Milieukontakt together with partners will stimulate initiatives to develop networking of the NGO community within countries and amongst countries in Eastern Europe.

3.4.2 Activities in Georgia

In George another approach was chosen based on the current reality and the needs and wishes of the community.

During the inception visit September 2005 the delegation managed to collect the information, both on stakeholders as on obsolete pesticides, necessary to develop a project plan for the project on obsolete pesticides in Georgia. The meeting was successful because of the many stakeholders and sites visited. Regarding civil society NGOs have capacity in all fields necessary to conduct the project; there are facilities, trainers and communication tools that can be used for the implementation of the project. Knowledge on obsolete pesticides is limited within the NGO movement and main source of information is the POPs team of the Ministry of Environment. Currently, Georgian NGOs working in the field of environment do not have their own national strategy meeting.

Obsolete Pesticides Management Specialist, Jan Betlem, (Tauw bv, the Netherlands) visited several smaller sites as well as the central storage site. Outcome of the visits to the sites are the following.

The inventory of locations and storages made on national level will needs elaboration in order to be able to starting on a regional scale. On certain locations visited there was a worrying situation with pesticides lying in open air and water. The availability of packaging materials in Georgia is certainly worth investigating since several different kinds of barrels were found in the country during the site visits. The NIP can set priorities on repackaging of obsolete pesticides, which can serve as further guidelines for the local project. A thorough overview on legislation and enforcement on pesticides in Georgia will be needed. The location of Kakhety was identified to implement a local project.

Observations made by the Ministry of Environment of Georgia are the following. The total of 214 sites has been checked in 12 regions of Georgia, out of which at 46 sites the contamination by pesticides was reported. Roughly estimated, the total amount of pesticides discovered is ~357 tons (plus 2,700 tons buried at Jagluji landfill). 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 laboratory has performed qualitative and quantitative analysis of the samples on POPs.

4. NEXT STEPS

In Moldova the Hincesti working group will develop a planning and implement the activities needed to collect, transport and repack the pesticides. This includes reconstruction work of the storage facilities, purchasing the repackaging materials and preparing necessary transportation. Support will be further provided by the expert to train the local teams on packaging and storage methods.

The local working structure will execute the action plan with the help of local and international experts. In addition the group will discuss possibilities for after care and remediation of the sites. The working group will organize Local Platform Meetings in order to promote their work and raise awareness amongst the public. Alternative methods in relation to the use of pesticides in agriculture will be discussed. Further they are developing plans to do fundraising for projects related to the central storage in the village Stolniceni and to start up working with the local people and farmers on pesticides.

In Georgia the location for the pilot project has been identified. Next steps to be prepared are the stakeholders analysis for the region Kakhety in order to be able to set up a local working group.

A working group with representatives of the government and from civil society organizations will function as core group to coordinate and steer activities regarding the first obsolete pesticide activities in Georgia.

The project will be extended towards Armenia in 2006. Further preparatory activities will start up for the organisation of the next HCH conference on pesticides.

Special developments are taking place at the 8th international HCH and Pesticides Forum where the Moldovan government has offered to host the next event in 2007. Milieukontakt has joined the preparatory committee.

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Initiatives in Moldova on obsolete pesticides www.vox.md

APPLICATIONS OF SPMDs AS A TOOL FOR ASSESSMENT OF PESTICIDES AND OTHER POPs IN WATER AROUND SPOLANA NERATOVICE IN 2002

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ABSTRACT

Organochlorinated pesticides belong to one of priority group of chemicals under the Stockholm Convention, consisting of a total group of 12 hazardous persistent organic contaminants (POPs), of particular concern to inventory and further reduction in all environmental compartments. The Semi-permeable Membrane Device (SPMDs) is commonly used for chemical and eco-toxicological monitoring and assessment in water and air, as a tool for passive sampling of those chemicals, together with others, such as polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenylethers (PBDE), etc. The SPMDs exposure is mostly considered as an integral concentration of those chemicals over the sampling period; SPMDs mimic bioaccumulation processes of Biomonitoring Organisms (BMOs).

SPMDs were used for assessment of POPa in the Czech Republic in many studies. One of the most important studies from 2002 focused on assessment of POPs release from Spolana Neratovice after a flooding. Spolana Neratovice produced chlorinated pesticides, mainly 2,4,5-T, HCB, and HCHs. The area of this chemical plant is highly contaminated by OCP, PCDD/F and PCB, which originated as byproduct of OCP production or chlorine production.

An assessment was made of surface water along the Elbe river basin, as well as of drinking water of individual suppliers (from wells). An evaluation of contaminations was also provided on background of routine monitoring (nowadays run on 15 rivers on 19 profiles), as part of biological monitoring realized by SPMDs, Dreissena polymorpha and fish, for evaluation of contamination trends. All deployments were performed within ≈30-days periods (integral response). Selected studies are used for demonstration of SPMDs applicability for assessment of POPs in drinking and surface waters.

Keywords: SPMDs, HCB, HCHs, POPs, toxicity.

INTRODUCTION

Undoubtedly, in recent periods, the most remarkable POPs source in the Czech Republic has been considered the Spolana Neratovice factory. Present contamination of POPs reflects production of some chlorinated pesticides (OCPs) in the 1960s, most of them chlorine herbicide 2,4,5-T, used by USA as "Agent Orange" in the Vietnam war. High amounts of PCDD/Fs was formed as a bi-product of 2,4,5-T production, particularly the most toxic 2,3,7,8-TCDD. Additionally, in 2002, another source of PCDD/Fs from chloralkali processes has been found and confirmed (1). This ran until the mid 1970s. However, despite termination of the OCPs production in the 1970s, OCPs and PCDD/Fs contamination has played the most important role for environmental acts in eliminating this hot-spot, confirmed by environmental measurements as well as the health problems of 55 workers, hospitalized mainly with severe chloracne (2). Since then, all contaminated buildings have been closed down. Today, remediation projects are prepared.

In 2002, a severe flooding episode in Bohemia also hit the Spolana factory, including buildings contaminated by

POPs. There was an expected dioxin and pesticide release into the whole flooded area, including individual water sources and soils, as well as the Elbe River. Immediately after the flooding, monitoring of POPs has been performed in all environmental compartments with the aim to evaluate the potential risk to the human population in this area.

One of the most important parts of the evaluation focused on the time trend of POPs contamination, based on evaluation data from pilot applications and routine monitoring by SPMDs, which mimics bioaccumulation of POPs in biota. Both selective POPs have been monitored (mainly OCPs, PCDD/Fs, PCBs), together with a selected set of eco-toxicological parameters, as complementary response of total contamination of non-polar, lipophilic chemicals dissolved in water. In this abstract, results of OCPs are presented in detail only.

MATERIALS AND METHODS

Materials and chemicals

From the list of POPs, these were analysed:

- OCPs: alfa- to delta-HCHs, HCB, o,p-DDT, p,p-DDT, o,p-DDE, p,p-DDE, o,p-DDD, p,p-DDD,
- PCDD/Fs: the 17 toxic congeners, given by WHO I-TEF, 1998
- PCBs: Tri-DecaCB (all detectable congeners).

All solvents were obtained from Merck (Darmstadt, Germany), purity LiChrosolv quality).

Sampling devices/equipment

Two sampling methods were selected for estimation of ambient water concentrations: grab sampling and sampling by SPMDs.

Grab sampling was performed in accordance with CSN EN ISO 5667 standards, with respect to particular requests of POPs. Water samples for OCPs determination were taken into 2 l dark glass jars, preliminarily rinsed by a combination of appropriate and validated washing procedures (water, organic solvents, etc.).

For passive sampling, standard SPMDs (purchased from ExposMeter AB, Sweden) were used, represented by lay flat thin-walled tube of nonporous, from LDPE, filled inside with 1 ml of synthetic lipid - triolein, neutral triglyceride (1,2,3-tri-[cis-9-octacenoyl]glycerol) of high purity (>97%). Dimension of the SPMD: width 2.5 cm (lay-flat), overall length 91 cm and wall thickness 75 -90µm, overall sampling area is about 460 cm2, total mass is about 4.5 g. Exploded view of overall SPMDs is given in Figure 1. Membrane contains transient pores with specific diameter approx. 10-9 m.

Common QA/QC criteria

Handling and processing of SPMDs was provided in a standard way, described previously (3). Membranes for deployment and after exposure were transported in airtight metal cans, in a cooler. Until any processing (before and after exposure), SPMDs were kept in a freezer at –20°C. For QA/QC, the transport field blanks were exposed during the sampler the whole installation and removal. These blanks were processed exactly as deployed samples and were used to describe maximal exposure of the SPMDs during transportation and handling. Moreover, fresh (not-exposed, from the same lot) SPMDs were processed through the whole sample pre-treatment and analytical procedures, reflecting storage and possible intake of POPs from chemicals and all used laboratory glassware.

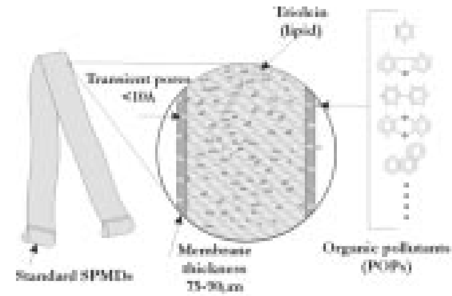


Figure 1. Exploded view of used SPMDs

SPMD deployment

Each SPMD was inserted and stretched in sampling racks (by means of hooks and spiral springs), put into protective shrouds (usually 3 SPMDs for chemical parameters and 1 SPMDs for toxicity assessment for 1 protective shroud were used) - see Figure 2. Temperature during exposure was monitored by T-data loggers (mounted on protective shrouds) with a time increment of 2 hours. The whole sampling system was put into a secured place. The depth below the water surface at which SPMDs were deployed had ranged from 80-120 cm. A period of each exposure was ≈30 days (in the autumn of 2002, after flooding, for Spolana assessment; in spring 2003 within the framework of routine monitoring).

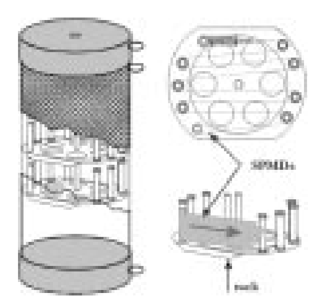


Figure 2. Sampling arrangement for SPMDs

Dialysis, analysis

After exposure, the surface of SPMDs was cleaned to remove surface film, and dialyzed with hexane in accordance with instructions in tutorial (3). Combined extracts from two membranes were spiked with isotope labelled internal standards of PCBs, PCDD/Fs. After spiking, extracts were cleaned up and analyzed by GC/MS/MS (4). The dialysate from the third membrane was split to equal aliquots. One for OCPs and PCBs analysis was spiked with isotopic labelled standards then cleaned up on H2SO4 deactivated silica gel column and analyzed by GC/MS/MS (GCQ and PolarisQ, Thermo Finnigan, San Jose, CA, USA). The second one was used for PAHs determination.

Estimation of ambient water concentration

Reporting of ambient concentration of compounds of interest in water was provided in accordance with equations below, in detail published recently (5-7). Time-averaged water-borne concentrations of OCPs were estimated from concentrations in exposed SPMDs. In general, the ambient concentration was derived from the following equation, derived from first order kinetics (describing general basic uptake of contaminant (i) in SPMDs.):

$$C_{S,i} = K_{SW}C_{W,i}(1 - \exp(-k_D t)) \qquad \text{Eq. 1}$$

where (kD) means dissipation (backward) rate constant, (CS) concentration in the SPMDs, (t) time of exposure, (CW) concentration in water, KSW= kU/kD is SPMDs-water partitioning coefficient, and (kU) means contaminant uptake rate (forward) constant.

From the equation, a situation was derived, relevant for OCPs exposure as Integrative sampling (linear uptake model). This is the case of short exposure time (?30 days) of highly hydrophobic compounds, where kD t<<1; then CS,i is given by:

$$C_{S,i} = K_{SW}C_{W,i}k_D t \qquad \text{Eq. 2}$$

In this case the CS,i increases linearly with time; exposure is driven by linear uptake model and sampling is integrative.
Using sampling rate parameter RS,I, is given by:

$$R_{S,i} = V_S K_{SW} k_D F_i \qquad \text{Eq. 3}$$

Sampling rate is in L.d-1, which can be understood as a volume of water (L), dialysed per day, and given temperature (t). Correction factor (Fi) is 1- fractional reduction in uptake flux, determined under defined conditions, due to bio-fouling impedance. For our cases, due to negligible bio-fouling surface layer after exposure was found, the Fi was denoted as 1.
Using sampling rate and concentration in water, combining previous equations, the ambient concentration was calculated from the following equation:

$$C_{W,i} = C_{S,i}V_S / R_{S,i}t \qquad \text{Eq. 4}$$

Sampling rates for ambient water concentration were used from publication, estimated for average of measured temperature, given in Table 1.

Table 1. Water sampling rates (Rs) at 10, 18, and 26 °C for OCPs

Compound	M ($g.mol^{-1}$)	Log K_{OW}	Rs (10°C) ($L\ d^{-1}$)	Rs (18°C) ($L\ d^{-1}$)	Rs (26°C) ($L\ d^{-1}$)
α-,β-HCH	290.8	3.86	0.9	1.4	1.8
γ-,δ-HCH	290.8	3.71	0.7	1.1	2.3
o,p'-DDE	318.0	5.56	2.3	2.4	6.0
p,p'-DDE	318.0	6.14	2.8	2.7	6.8
o,p'-DDD	320.1	6.08	2.5	2.3	5.5
p,p'-DDD	320.1	5.75	2.3	2.5	6.1
o,p'-DDT	354.5	5.59	2.0	3.3	4.0
p,p'-DDT	354.5	5.47	2.0	3.7	4.1

Source: Huckins et al. (2002)

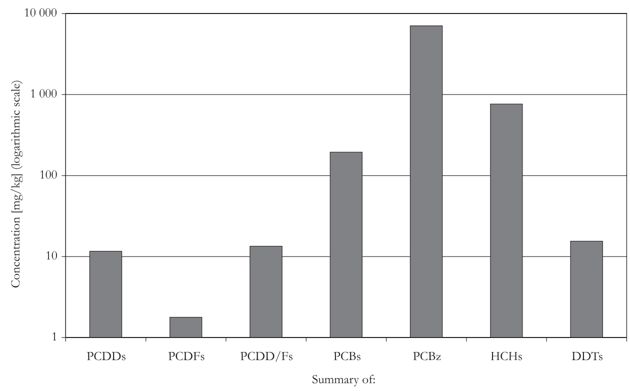
RESULTS AND DISCUSSIONS

As noted previously, of special importance to any monitoring is thorough identification of the contamination profile yield by relevant compounds found in Spolana. These are given in Graph 1. It is noteworthy that the concentration axis is in logarithmic scale. From an overall composition of compounds, we have found a dominant concentration of OCPs in dust from contaminated building no. A 1420 (considered one of the most contaminated objects, as described earlier).

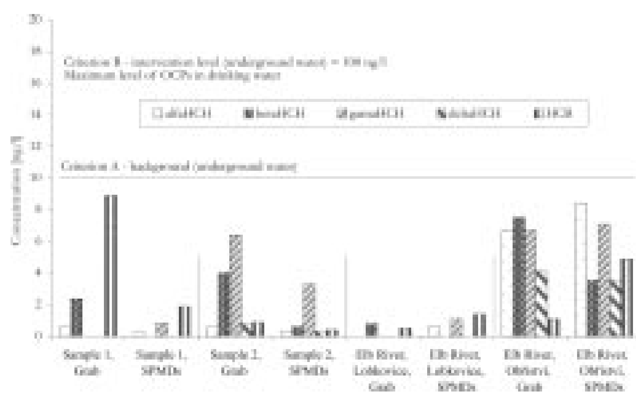
Assessment of drinking water

Various individual water sources (wells) were selected for the OCPs (and other POPs) assessment, based on a sampling plan. Two sampling methods were selected for estimation of ambient water concentrations, as noted previously. Quantitative levels were compared with the following legislation:

- Methodical direction of Ministry of Environment, for underground water and soil, from 1996.
- Regulation Act No. 376/2000, Ministry of Health.



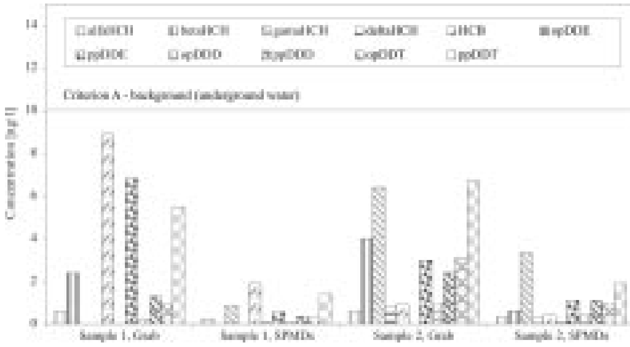
Graph 1. A profile of POPs (from the building A 1420)



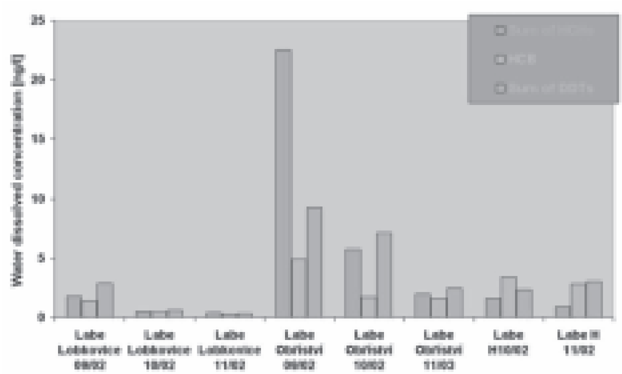
Graph 2. Contamination profiles (grab and SPMDs sampling)
Sample 1 and 2 – drinking water from individual supply
Elb River Lobkovice – the profile before Spolana
Elb River Obøíství – the profile after Spolana

Small portion of results (Sample 1, 2) is given in Graph 2. It represents all measured results found below Criterion A. Both quantitative levels and qualitative representation (fingerprinting) were evaluated.

As expected, due to high amounts water, no remarkable contamination of drinking water has been found; concentrations were below the background-control limit 10 ng/l (see Graph 2). This conclusion is derived from quantification, which has been confirmed using both sampling methods. As expected, results from grab sampling exhibited higher values, most probably given by analysing all forms present in water (soluble and non-soluble fractions, bounded into micro-particles), whereas SPMDs has sequestered only truly water-dissolved fractions.



Graph 3. Contamination patterns of OCPs



Graph 4. Trends of contamination on Elbe River
Labe = Elb River
Labe H = the profile in the Czech-German border

In spite of different quantitative results, a comparison of both methodologies has shown very good agreement in trends and qualitative profiles (see Graph 2). Graph 3 shows the relevance of all monitored OCPs (HCHs, HCB and DDTs and its metabolites), which complies with all findings in Spolana.

Assessment of surface water

Quantitative levels were evaluated according to the methodical direction of the Ministry of Environment, as stated above. From Graph 2, there is an apparent elevated level of HCHs and HCB behind the Spolana at Obříství profile, whereas low contamination has been found in the Lobkovice profile (before Spolana). Evaluation of the contamination pattern from Spolana shows that this can be considered as the contamination source. However, a definite conclusive statement on the origin would require additional sampling of other potential sources. On the other hand, if no additional source has been identified so far, an elevated concentration can confirm evidence of OCPs point source from Spolana, although concentrations are below Criterion A of the methodical direction. Moreover, Graph 4 shows an apparent decreasing tendency of OCPs, which can be caused by partial release from contaminated soils and sediment and thus makes it also possible to explain the elevated concentration found immediately after the flooding.

CONCLUSIONS

The assessment of POPs around Spolana Neratovice has been a very complex study, due to long-term sampling, range of assessed parameters and complexity of characteristic patterns on which particular sources of contamination could be identified. Thus, conclusions are focused on OCPs only.

SPMD prove to be a very effective tool for POPs assessment of drinking water (individual sources) and surface water. Results have shown good reproducibility data for OCPs, if comparing the grab and passive sampling methodologies, falling into the range of the same order of magnitude. However, fingerprints grab and SPMDs are not generally comparable.

Based on the isomer pattern of HCHs and DDTs, it is possible to identify Spolana as the potential source of OCPs in drinking water, although historical use of those compounds must be taken into consideration to confirm this hypothesis.

Both quantitative and qualitative (fingerprinting) profiles were identified by SPMDs, as integral response to truly dissolved OCPs in water.

As for surface water, due to an elevated concentration in the profile downstream Spolana, the contamination source can be determined just for this source.

Results of SPMD sampling exhibit lower values than those from grab sampling (due to accumulation of truly dissolved chemicals only).

To help in identification of pollution sources, multivariate data analysis approach is needed for the most complex interpretation, which is over the scope of this contribution and is subject of special publication, including evaluation response sequestered chemicals on selected toxicity test.

Due to a relatively large amount of available calibration data for OCPs, SPMDs shows a promising tool for both screening and monitoring of this group of chemicals, with the complementary role in appropriate tests on combinations of toxicity.

ACKNOWLEDGEMENTS

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ORGANOCHLORIDE PESTICIDES BLOOD LEVELS IN THE POPULATION OF CIDADE DOS MENINOS, DUQUE DE CAXIAS COUNTY, RJ, BRAZIL: PRELIMINARY RESULTS

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ABSTRACT

Antecedents

In the early sixties, a pesticides factory producing HCH, DDT and other organochloride compounds located in Cidade dos Meninos, a rural settlement in the state of Rio de Janeiro, Brazil, stopped its production. Several thousand tons of pesticides remained in the facilities without major control procedures, and were used in agriculture by the population living around the factory. A chemical remediation of the contaminated area carried out in 1994 has failed, and other volatile compounds were introduced in the area.

Objectives

To ascertain the blood organochorine pesticide levels in the population living in Cidade dos Meninos area.

Methods

Blood samples were collected from all 1367 persons either living or formerly living in Cidade dos Meninos, and a questionnaire filled with data on personal and lifestyle (diet, reproductive antecedents, breastfeeding, other) exposures. Blood levels of selected organochlorine pesticides (HCH, DDT, DDD, DDE, Aldrin, Dieldrin, Endrin, HCB, Heptachlor, Trans nonachlor, Chlordane, Endosulfan, Methoxychlor and Mirex) were ascertained by electron capture chromatography. A cut-off of 20ng/mL was used as indicating organochloride high exposure. This paper presents the preliminary results from a sample of 295 participants in the survey, which was approved by the Oswaldo Cruz Foundation Ethical Committee.

Results

Median DDE levels among adults were 19.64 ng/mL (47% with levels higher than 20 ng/mL) and median beta HCH levels were 8.73 ng/mL (28.8% with levels higher than 20 ng/mL).

Discussion

The observed high blood levels of DDT and HCH suggest the need of a meticulous clinical and epidemiological follow-up of the studied population.

Key-words: HCH, DDT; Aldrin; organochlorine, pesticide; Brazil.

INTRODUCTION

Hexachlorocyclohexane (HCH) exposure can occur by inhalation in the occupational set wherein it is produced, or in a non-occupational set such as observed near HCH industrial plants or rural plantations following its use in agriculture as insecticide (Jung et al., 1997). Besides inhalation, HCH exposure may also occur towards the intake of contaminated food (milk, meat, seafood and vegetables) or water subsequent to underground reservoirs contamination. (WHO, 1991a,b,c,d; Agency For Toxic Substances And Disease Registry, 1995).

Main acute effects include convulsions, but also skin, muscle, cardiovascular and gastrointestinal disturbances. In animals, liver, kidney, central nervous system and immune system effects have been reported following HCH exposure (Environmental Health Protection Agency, 2001).

Chronic effects following HCH exposure include suspicion of cancer in animals, mainly alpha-HCH and limited evidence for beta and gamma isomers, and cardiovascular, immune, nervous system disturbances (Braham, 1994; Karmaus & Wolf, 1995; Joshi et al., 1996; Environmental Protection Agency, 2001).

In the early sixties, a factory producing HCH, DDT and other organochlorine pesticides was closed. The factory was in the rural village of Cidade dos Meninos, Duque de Caxias County in the State of Rio de Janeiro, Brazil. Several tons of HCH

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remained in the area, and HCH was further used in agriculture and for other purposes by local settlers until 1994. At this time, a chemical remediation was carried out by the government.

Nevertheless, suspicion of organochlorine contamination in the local population remained. Therefore, a survey to ascertain organochlorine serum levels in the local population was carried out, and this paper presents the preliminary pesticide distribution levels in Cidade dos Meninos.

METHODS

In ascertaining organochloride serum levels among Cidade dos Meninos inhabitants, a survey was carried out between November 2003 and March 2004. Blood samples were collected from 1,367 persons either living, or formerly living, in Cidade dos Meninos, and a questionnaire filled with data on personal and lifestyle exposures such as diet, reproductive antecedents, breastfeeding and others factors where obtained through personal interviews.

Blood levels of selected organochlorine pesticides (alpha-HCH, beta-HCH, gamma-HCH, DDT, DDD, DDE, Aldrin, Dieldrin, Endrin, HCB, Heptachlor, Trans nonachlor, Chlordane, Endosulfan, Metoxychlor and Mirex) were ascertained by electron capture chromatography.

This paper presents the preliminary results from samples of 295 participants in the survey. Organochloride plasma levels are presented stratified by age in two groups, children (0-14 yrs. old) and adults (15 yrs. or older). All participants gave their written consent to be enrolled in the study, which was approved by the Oswaldo Cruz Foundation Ethical Committee.

RESULTS

Organochloride residues were observed in all participants whose blood samples were analyzed, and are presented in table 1 (adults) and table 2 (children). Identified median alpha-HCH levels among adults were 2.54 ng/ml, while beta-HCH median levels were 8.73 ng/ml. According to DDT exposure, median p-p´ DDT levels among adults were 6.44 ng/ml, while DDE median levels were 39.53 ng/ml. Observed median levels for Aldrin were 17.5 ng/ml. High exposure (20ng/ml or higher) to these organochloride substances was observed for DDE in 47.6% of the adults and 28.8% for beta-HCH.

Quite similar trends were observed in the samples of children. Median levels of alpha-HCH in the studied sample were 5.31 ng/ml, 8.30 ng/ml for beta- HCH, 11.77 ng/ml for p-p´-DDT, 13.98 ng/ml for DDE and 30.22 ng/ml for Aldrin. High exposure levels (20 ng/ml or more were observed for DDE (42.5% of children), Aldrin (64.5%), p-p´-DDT (33.9%) and beta-HCH (29%).

Table 1 – Blood organochlorine pesticide levels, 15 yrs. or older, Cidade dos Meninos, Duque de Caxias, RJ, 2005 (233 participants)

Pesticide	25th percentile (ng/ml)	50th percentile (ng/ml)	75th percentile (ng/ml)	Maxim value (ng/ml)	> 20 ng/ml (%)
Alpha HCH	1.10	2.54	6.03	85.75	5.6
Beta HCH	4.46	8.73	21.82	197.16	28.8
Gama HCH	0.39	0.82	2.08	17.45	-
p-p´DDD	0.49	1.02	1.82	11.60	-
o,p´ DDT	0.00	0.49	1.47	12.22	-
p p´ DDT	2.99	6.44	10.79	91.60	9.4
p-p´-DDE	6.99	19.64	39.53	840.28	47.6
HCB	0.18	0.31	0.58	138.00	-
Heptachlor	0.00	0.19	0.78	11.30	-
Alpha Chlordane	0.00	0.21	0.46	9.21	-
Gama Chlordane	0.00	0.13	0.40	8.35	-
Aldrin	11.16	17.05	24.97	110.67	39.9
Endrin	0.33	0.77	1.53	15.25	-
Dieldrin	0.30	0.58	1.04	11.61	-
Endosulfan1	0.00	0.23	0.44	6.92	-
Endosulfan2	0.16	0.45	1.17	14.74	-
Trans nonachlor	0.17	0.36	0.70	8.38	-
Methoxychlor	0.00	0.33	0.80	2.83	-
Mirex	0.39	0.87	1.73	15.96	-

Table 2 – Blood organochlorine pesticides levels, 0-14 yr, Cidade dos Meninos, Duque de Caxias, RJ, 2005 (62 participants)

Pesticide	25th percentile (ng/ml)	50th percentile (ng/ml)	75th percentile (ng/ml)	Maxim value (ng/ml)	> 20 ng/ml (%)
Alpha HCH	2.38	5.31	15.61	77.24	19.4
Beta HCH	4.76	8.30	24.55	424.81	29.0
Gama HCH	0.66	1.55	4.56	16.82	-
p-p´DDD	0.97	1.77	3.02	15.85	-
o,p´ DDT	0.00	0.53	1.80	12.09	-
p p´ DDT	4.20	11.77	24.90	59.72	33.9
p-p´-DDE	5.87	13.98	38.39	276.13	42.5
HCB	0.27	0.55	0.93	6.10	-
Heptachlor	0.00	0.47	1.38	11.00	-
Alpha Chlordane	0.25	0.45	1.26	7.22	-
Gama Chlordane	0.00	0.26	0.76	9.90	-
Aldrin	15.94	30.22	78.96	169.14	64.5
Endrin	0.75	1.53	3.37	18.94	-
Dieldrin	0.52	0.95	2.15	12.32	-
Endosulfan1	0.00	0.33	0.84	6.37	-
Endosulfan2	0.42	0.91	2.29	25.51	-
Trans nonachlor	0.30	0.60	1.41	7.33	-
Methoxychlor	0.00	0.44	1.50	8.21	-
Mirex	0.33	1.17	2.56	12.92	-

DISCUSSION

As chemicals which are deposited in the fatty tissue, organochlorine pesticides remain observed for long time in organic tissues of humans and other species. This can be exemplified by DDT, whose use in agriculture was forbidden in Brazil in 1985, but remained employed in public health activities, such as malaria control, until the late 1990s. In this sense, high DDE levels, reflecting past exposure to DDT, have been reported by different toxicological studies carried out in Brazil. Nevertheless, DDE levels observed in this survey are higher than those reported by other studies in the general population in the same state of Rio de Janeiro, wherein Cidade dos Meninos is located (Paumgartten et al., 1998).

On the other hand, this is not the case of HCH, which has not been reported in studies carried out in the general population of Rio de Janeiro and in other areas in Brazil (Mendonça et al., 1998). This fact seems to reinforce the suspicion that the observed high levels of HCH contamination ascertained in this study indeed reflect local contamination from the old pesticide factory remains in Cidade dos Meninos.

The ascertained organochlorine levels among participants in this study are several times higher that those used as reference values by the National Environmental Safety Agency in Germany (Ewers et al, 1999): 0.1 μg/l for alpha-HCH in the blood of adults and children, compared to median levels of 5.31 ng/ml in children and 8.73 ng/ml in adults observed in our survey. A similar trend was seen for beta-HCH, with reference blood levels in Germany ranging from 0.3 μg/l at age 7-10 yrs. to 2.0 μg/l for those aged 65 yrs. or more, compared to the median levels of 8.73 ng/ml in adults and 8.30 ng/ml in children at Cidade dos Meninos.

High median levels of Aldrin, a chemical which was not originally produced in the old pesticide factory in Cidade dos Meninos, were observed in this survey. These measurements were obtained by chromatography, an analytical tool used to separate chemical substances. Nevertheless, mass spectrography, a more accurate methodology allowing substances identification, could not be performed in this study. In this sense, current results suggest the presence of Aldrin in a large number of participants, including children, but they should be confirmed by further analysis.

CONCLUSIONS

High levels of exposure to HCH, DDT, DDE and Aldrin were observed in the preliminary analysis of blood samples of 295 participants during a population survey carried out in Cidade dos Meninos, Brazil.

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HEALTH EFFECTS OF PESTICIDE APPLICATION

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ABSTRACT

Pesticides alongside with certain chemicals exert after-effects even at the lowest levels and are known to cause cancer and allergy. Application of tumor markers as screening tests allows detecting cancers early and often leads to more effective treatment with fewer side effects.

Our aim was to reveal influences of the environmental pollutants on health among urban, rural and remotely settled population.

Screening investigation method was applied to study the frequency of allergy and oncology occurrence in the Republic of Armenia.

Population groups involved patients from:

✓ agricultural districts with intense pesticide application (Group 1),

✓ industrial regions (Group 2),

✓ mountainous regions of cattle-breeding without pesticide application (Group 3).

Enzyme Immunoassay (EIA) was used and the following tumor markers:

• Cancer antigen CA242 – the latest generation marker of colorectal and pancreatic cancer;

• Carcino Embryonic antigen (CEA) – marker for gastrointestinal and colon cancer;

• Cancer antigen CA19-9 EIA as a useful marker for differentiation between malignant and benign pancreas disease.

Immunoglobulin E (IgE) marker of allergy was used to reveal the allergic reactions.

The screening investigation revealed that:

➔ incidence of gastrointestinal cancer corresponded to country average statistical data;

➔ there was an increase in occurrence of colorectal and pancreatic cancer in Group 1 and Group 2, compared with Group 3;

➔ pancreatic cancer prevailed in inhabitants of Group 1;

➔ levels of IgE were significantly higher in Group 1, compared to Groups 2 and 3;

➔ more asthma cases were registered in children of Group 1 patients.

Complex use of tumor markers CA19-9 and CA242 allows to perform differential diagnosis of colorectal and pancreatic cancer and serve as a tool to reveal specific effects of chemicals, including organochlorine pesticides, nitrates, etc. On the other side, IgE is a confidential and applicable tool for reveling allergic after-effects caused by agrochemicals.

Key words: pesticides, allergy, cancer, tumor markers, Immunoglobulin E

INTRODUCTION

It is well known that pesticides may be encountered as residues in food, air, water and soil. People may also be exposed to pesticides used in agriculture, applications for pest control at home or at work, applications to roadside right-of-ways to control weeds and applications of pesticides for public health vector control programs. For example, exposure to pyrethrum can trigger an asthma attack at a trivial dose of exposure.

In agriculture of Armenia, likewise any other country, there is a constant use of pesticides, nitrogen fertilizers, and plant protectants. These chemicals contain many agents inducing allergy and cancer. Numerous chemicals though not belonging to the class of direct carcinogens, even at minute doses in living organism can undergo metabolic changes and produce carcinogenic effect. If the organism is exposed to the allergen, allergic reaction develops followed by chronic inflammation. In this phase, excretion of inflammatory mediators can be induced not only by the specific allergen that has triggered the reaction, but also by unspecific stimuli, e.g. chemicals (pesticides, formaldehyde, and phenol). A specific pesticide exposure, which might cause an allergic reaction in a susceptible individual can be 1,000 times less than an exposure, which would cause a toxic reaction. An allergen stimulates the organism to produce specific antibodies belonging to Immunoglobulines class E (IgE). Therefore we used IgE determination for diagnosing allergy reaction induced by chemical agents.

Usually, agricultural workers are aware that pesticide irritation means problems with skin, eyes, or respiratory tract, but it is more important to understand that pesticides alongside with certain chemicals exert after-effects even at the lowest levels and are known to cause allergy and immunity disorders, affect the hepatic and digestive tract, and, in the long-run, bring forth oncology problems.

Our aim was to reveal the influence of environmental pollutants on health in urban, rural and remotely settled population. Application of tumor markers as screening tests allowed detecting cancers at early stage and often leads to more effective treatment with fewer side effects.

MATERIALS AND METHODS

Screening investigation method was applied to study the frequency of oncology diseases occurrence in the Republic of Armenia.

Population groups involved patients from different regions of Armenia.

Group 1 comprised inhabitants from agricultural districts with intense pesticide application. Group 2 involved population from industrial regions and Group 3 was represented by dwellers of mountainous regions of cattle-breeding without pesticide application.

Enzyme Immunoassay (EIA) was used and the following tumor markers:

- Cancer antigen CA242 – the latest generation marker of colorectal and pancreatic cancer;
- Carcino Embryonic antigen (CEA) – marker for gastrointestinal and colon cancer;
- Cancer antigen CA19-9 EIA as a useful marker for differentiation between malignant and benign pancreas disease.

Immunoglobulines IgA, IgG, IgM and IgE as markers of humoral immunity and allergy were also used.

RESULTS AND DISCUSSION

Our screening investigation revealed that:

1. the incidence of gastrointestinal cancer in tested population corresponded to average statistical data in country total population;
2. there was an increase in occurrence of colorectal and pancreatic cancer in patients from agricultural districts with intense pesticide application (Group 1) and industrial regions (Group 2), compared to dwellers of mountainous regions of cattle-breeding without pesticide application (Group 3);
3. the analysis of results obtained in concern of patients addressing oncology medical institutions demonstrated that pancreatic cancer prevailed in Group 1 (inhabitants of rural districts, where pesticides were applied);
4. levels of IgE were significantly higher in Group 1, compared to Groups 2 and 3;
5. more asthma cases were registered in children of Group 1 patients.

Complex use of tumor markers CA19-9 and CA242 allowed us to perform differential diagnosis of colorectal and pancreatic cancer and served as a tool to reveal specific effects of chemicals, including organochlorine pesticides, nitrogen fertilizers, etc.

Usually tumor markers are used for diagnosis and monitoring of disease follow-up in practice of clinical investigations. We showed that tumor markers can be applied as screening method at early stage of disease development under various unfavourable factors, in particular under the impact of pesticide exposure.

At the same time we studied the indices of humoral immunity: immunoglobulines A, M and G (IgA, IgM, IgG). To our view, the most interesting finding was elevation of IgG only in patients from Group 1. Probably, in this Group the general immunity is lower as compared to Groups 2 and 3.

The probability, whether some types of immune response are responsible has been debated at length. Some authors have claimed that an alteration in immune responses is initiated by some “immunotoxic” event, leading to excessive sensitivity of individuals to minute amounts of chemical in their environment (including some pesticides) resulting in the oncology states, aller gy-related disorder, “multiple chemical sensitivity” (MCS) syndrome, chronic fatigue syndrome, etc.

Further screening investigation would undoubtedly help us to reveal the role of environmental and other factors in the development of carcinogenesis and, as a result, to work out and take measures to prevent allergy and oncology disease states prevalence.

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THEME VI: WASTE MANAGEMENT

DEVELOPMENTS ON TECHNICAL GUIDELINES FOR OBSOLETE PESTICIDE MANAGEMENT

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INTRODUCTION

One of the major outputs of the FAO programme on obsolete pesticides has been a serries of guidelines aimed at developing countries. The purpose of the guidelines has been to provide practical advice on how to deal with various aspects of obsolete pesticide elimination and how to prevent future accumulation of obsolete pesticides through better pesticide management and reduced reliance on pesticides.

Existing guidelines deal with the following issues:

- Prevention of Accumulation of Obsolete Pesticide Stocks
- Pesticide storage & stock control manual
- Disposal of bulk quantities of obsolete pesticides in developing countries
- Management of small quantities of obsolete and unwanted pesticides
- Assessing soil contamination: a reference manual
- Baseline study on the problem of obsolete Pesticides
- Training Manual on inventory taking obsolete pesticides
- Country guidelines.

The process of updating existing and developing new guidelines and tools to assist developing countries and countries with economies in transition to eliminate and prevent obsolete pesticides is continuous. The following documents and tools are currently in development:

- An update of the guidelines on Disposal of bulk quantities of obsolete pesticides in developing countries
- Environmental Management Toolkit
- Addition and revision of training modules on environmental risk assessment, safeguarding (repackaging) and inventory of obsolete pesticides
- Inventory database to manage all inventory data and provide a comparative risk assessment of storage sites
- Container management guidelines.

This paper focuses on two of the guidelines in development and provides a detailed outline on their structure and mode of use.

NEW DISPOSAL GUIDELINES

FAO first published guidelines on the disposal of bulk quantities of obsolete pesticides in 1996. Since that time technology has advanced, new regulatory mechanisms such as the Stockholm Convention on POPs have been developed, and much experience has been gained in operations to dispose of obsolete pesticides and other hazardous wastes from developing countries and countries with economies in transition. There is therefore a clear need to revise the existing guidelines.

- The new version will provide guidance for the disposal of obsolete pesticides as well as contaminated containers and packaging and contaminated soils. The guidelines will rely on accepted international standards as benchmarks for suitable disposal options in order to ensure that no sub-standard solutions are recommended. In addition, only technologies proven for pesticides destruction will be included.

The principles of good waste management are applied to the guidance. This is based on the 3-Rs: Reduce, Reuse, Recycle. Only after these options have been applied to their maximum potential is disposal considered. In addition the requirements of the Basel Convention are also applied. These call for environmentally sound management of hazardous waste, and the application of the *Proximity Principle* which requires hazardous waste to be dealt with as close as possible to its source.

However, obsolete pesticides often cannot be considered for reuse since they may be banned. Where products are still permitted for use, tests for their reusability are complex and costly and therefore only viable if large quantities of a given material in good condition are found. Recycling of obsolete pesticides is also technically complex and highly dependent on the physical and chemical properties of materials as well as on the availability of appropriate facilities. Quite often destruction represents the least cost and least risk option.

The guidelines contain step by step processes for selecting the most appropriate disposal option. They include descriptions of the available recycling and disposal technologies which provide information about the capabilities of each technology and their strengths and weaknesses. Opportunities for managing wastes in locally available facilities are explored including the use of existing local facilities, and the creation of new local facilities. In addition exportation to existing facilities abroad is explored as an option. The mechanisms used for decision making include flowcharts, decision trees and matrices to assist in selecting disposal options and there is a comprehensive legislation matrix that takes into consideration what is permitted.

A step by step flowchart guides countries through the recommended steps required for disposing of obsolete pesticide stocks. This is based on extensive experience of implementing such projects in different regions. The three key areas addressed are institutional, evaluation and planning, and implementation. The flowchart includes steps for establishment of a project steering committee and management unit, execution of an inventory (for which guidance is being prepared in a separate document), review and feasibility studies for disposal options and implementation of the selected option.

An example of the treatment options considered is provided in the table below:

Disposal Processes

	Handling, Repackaging & Preparation	Pre-Treatment	Destruction	Residue Disposal
Pesticides	• Bulking • repackaging • separation of liquid and solids	• Thermal desorption • Fuel blending • Cement kiln • B C D • G P C R • Plasma-A rc	• High temperature incineration	• Landfill (ash, solid residues • scrubbing (gas emissions) • effluent treatment (scrubbing liquors)
Soils	• excavation	• Solidification • vitrification • grading and screening • washing[2] • thermal desorption[2]	• chemical reduction • biodegradation	• Landfill • long term storage
Containers	• Puncturing • shreddin g • crushing	• Washing[2]	• Smelting metals • f uel for com bustion process • recycling of plastics	• Reuse of recycled materials • Landfill of unusable com ponents

In addition to flow charts, decision trees are used which guide users through the decision process, provide clear criteria for making decisions and are linked to the disposal options matrix as illustrated above but which also match a pesticide's chemical characteristics to disposal options.

Summary

The new revised guidelines will be an update of existing FAO guidelines on destruction of bulk quantities of obsolete pesticides. They are based on extensive practical experience and make links with related initiatives and documents. Prior to publication they will be peer reviewed and it is expected that they will be published in early 2006.

ENVIRONMENTAL RISK ASSESSMENT

The second of the guidelines and tools under development that was presented in some detail at the 8th HCH and Pesticides Forum is entitled the Environmental Management Tool Kit (EMTK). This has been developed in response to needs identified during the implementation of several obsolete pesticide projects, and provides a practical approach aimed at achieving successful project implementation and execution

Why do we need an EA tool?

As mentioned, this tool has been developed specifically in response to needs identified during the implementation of projects for the elimination of obsolete pesticides in less developed countries. It is field based in that it is designed as a tool which uses field data to provide outputs that are useful in planning field activities. It is also specifically geared to working with obsolete pesticides and POPs pesticides. It is designed for use in less developed countries and is simple and robust with no over-complication of technical issues. The system is also designed to provide useful and practical outputs that can help countries in the implementation of operations to eliminate obsolete pesticides.

The EMTK aims to minimize subjectivity in risk assessment and risk based decision making by providing a standardized approach based on actual field data. Country teams are trained to collect the relevant data that can then be used to provide a risk factor for each pesticide storage facility. The outputs of the system provide a risk-based framework that can be used in the planning and implementation of operations to collect, safeguard, store and transport obsolete pesticides and POPs.

There are four main components of the EMTK:

1. Prioritisation of stores based on RISK to public heath and environment - The risk factor allocated to a store takes into account the store contents, the condition of the store and the location of the store in relation to its environment. The output of this tool is represented graphically so that an easily understood representation easily allows decisions to be made on prioritization of action based on risk.

RF (location)

Sensitive location	High Priority Stores
Lower Priority Stores	Bad storage conditions

RF (store)

2. Selection of proposed collection centres - The intention of this tool is to identify locations and buildings that can be used during obsolete pesticide disposal operations to centralize stocks on an interim basis before they are transported to treatment facilities. Once an environmental assessment of a potential collection point has been completed, a logistical assessment is carried out, followed by a political and public assessment that takes into account local planning requirements. There may be no perfect locations for centralization, in which case the improvements needed in order to meet specifications and expectations can be identified, and the necessary work programmed. The intention of this expertise is to use available facilities where possible, but to ensure that appropriate high standards of health and safety and environmental protection are applied.

3. Safe transport of materials to collection points - Transport of hazardous materials increases risk and certain measures must be taken to avoid or mitigate risks. The transport tool takes steps to identify potential risks that will be used and guides users to select least risk options and to apply procedures that will maximize risk reduction and mitigation where necessary. The transport tool is based on the UN-ECE ADR (European Agreement for Carriage of Dangerous Goods by Road), but it is not necessarily expected that countries will adopt the recommended regulations wholesale.

Nevertheless, the tool advises route planning for risk minimization and on minimum standards for:

- Vehicles
- Security / escorting of the transport
- Spill intervention
- Emergency plan
- Driver training

4. Management and storage of waste materials - this tool is based on:

- Council Directive 96/82/EC (Seveso II) - mainly addresses planning issues
- FAO Guidelines on pesticide storage and stock control
- GIFAP/GCPF/CLI guidance

Interim storage recommendations cover the segregation of materials as well as emergency planning and response including reporting requirements. Again, it is not necessarily anticipated that countries will adopt the regulations and recommendations on which the tool is based wholesale, but that they will be used selectively as relevant to the specifics of the country and the operations being executed.

Summary

The EMTK covers a diverse set of subjects as described above, but all of these are interlinked and therefore their integration into a single manual or toolkit has been deemed useful by countries that have worked with it. The toolkit is divided into the discrete components that can be applied individually. Their comprehensive application to obsolete pesticide disposal operations provides and effective environmental management plan.

The system has been developed in conjunction with countries and has already been applied in some situations. Its more extensive use, for example in countries participating in the Africa Stockpiles Programme will provide a valuable testing ground and will probably lead to iterative developments.

OBSOLETE PESTICIDES MANAGEMENT IN UKRAINE, BELARUS AND RUSSIA

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Financed by the Danish Government under the organisation DANCEE (Danish Ministry of the Environment, Danish Environmental Protection Agency) COWI has carried out three major obsolete pesticide projects during the last 5-10 years in Eastern Europe. A schematic reporting from these projects can be seen below. If further information is needed please contact J. Lauridsen by mail (JQL@COWI.DK.)

The project titles are:

- Elimination of Risks Related to Stockpiled Obsolete Pesticides (OP) in Ukraine, 1998-2005
- Management and Disposal of Accumulated Obsolete Pesticides in Belarus, 1999-2005
- Environmentally Sound Management of Stocks of Obsolete Pesticides in Russia, 2004 & 2005

UKRAINE

Phase I

- Finished in 2000 with a national plan
- 15-22.000 tons of obsolete pesticides (OP) have been identified
- The OPs are stockpiled under unsuitable conditions
- Preparation of catalogue of disposal options, etc. etc.

Phase 2A

- Reconstruction of obsolete pesticide storage in LOZOVAYA – a pilot project
- Collection of 160-200 tons of obsolete pesticides in the Lozovaya rayon.
- Training of staff from National Centre for Hazardous Management (NCHWM) and from Oblasts in Pesticide Management
- Training people from the National Centre of Hazardous Waste Management (NCHWM) in business plans development

- Implementation of a Geographic Information System (GIS) for registration of the storages
- Implementation of a database for pesticide inventory in NCHWM in Kiev
- Carried out English courses for more than 30 persons in Kiev and Kharkiv
- Carried out public awareness and information campaign
- Conducted a seminar for environmental authorities with participants from all 26 Oblasts

Phase 2B

- Training-demonstration duplication of collection, re-packing and storage of obsolete pesticides to interested oblasts in Ukraine
- Result: More than 1000 tons of OPs have been collected and stored at safe local storage facilities in 13 rayons spread over six oblasts and the Autonomous Republic of Crimea

BELARUS

Project results

- Report on evaluation of risk level of obsolete pesticides in Verkhnedvinsk landfill
- Repacked and stored more than 280 tons of obsolete pesticides in Slutsk in Minsk oblast and more than 1180 tons in Zelva and Smorgon in Grodno oblast. Grodno oblast is nearly cleared of out-of-control obsolete pesticides lying around.
- Report on final destruction methods has been finalised and will be reported later today.
- The public information campaign has been a big success, with many newspaper articles, brochures, school competitions, public consultations and radio- and television broadcastings.
- Official guidelines on how to handle obsolete pesticides in the future have been prepared based on the results of this project.
- An electronic database containing information of the collected obsolete pesticides has been made (including e.g. pick-up spots, target depots and exact amounts) and has been handed over to Ministry of Environment for future updating.
- A folder presenting the project has been produced and distributed.

RUSSIA

Project Objectives

- Prepare inventories of OPs;
- Develop action plans for future management and disposal of OPs; and
- Demonstrate safe and environmentally sound management of obsolete pesticide stockpiles.

In this project we work with

- Organisation of authorities (Federal, Oblast, Dept, NGO, etc.)
- Identification of acceptable storage facilities
- Public Participation
- Inventory work 2004
- Action Plan work
- Collection and repackaging
- Preparation of an economic model of the work for future use.

The project is running well, and the final reporting might be part of the next HCH-meeting.

In the last 10 years COWI has worked with Obsolete Pesticides in the following projects:

- Review on Obsolete Pesticides in Eastern and Central Europe, DANCEE 2001
- Status on POPs in the Russian Federation; DANCEE 2002
- Obsolete Pesticides – Status in the Candidate Countries; EC_DGE 2002
- Supervision Disposal of Pesticides, Albania; Phare 2002-2003
- Management and Disposal of Accumulated Obsolete Pesticides in Belarus; DANCEE 1997 - 2005
- Elimination of Risks Related to Stockpiled Obsolete Pesticides in Ukraine, DANCEE 1998 - 2005
- Environmentally Sound Management of Stocks of Obsolete Pesticides in the North West Region of Russia; DANCEE 2004-2005
- Review of POPs Non-incineration and Incineration Technologies; DANCEE 2003-2005
- Interim Guidance for Development of National Implementation plan for (the POP's in) the Stockholm Convention, DANCEE, 2003.

MANAGEMENT OF OBSOLETE PESTICIDE CLEANUP IN ROMANIA

Neel Stroebaek

Ramboll Denmark

PRESENTATION OF THE PESTICIDES DISPOSAL PROGRAM IN ROMANIA

The Pesticide Disposal Program in Romania operates over the period December 2004 – July 2006 and involves 1,409 tonnes of obsolete pesticides spread over 133 locations in Romania. It is one of the largest cleanup projects of its kind in Europe to date, based on a professional FIDIC Contract Framework and high-quality implementation routines. A new strategy for obsolete pesticides prevention through agreements with the Industry is also in preparation.

Romania does not have sufficient capacity to destruct and/or neutralise obsolete pesticides, but with the funding from the EU Phare program, and co-funding from the Romanian Government, it is possible to clean up these sites and transport the obsolete pesticides to Germany for destruction.

ACTORS AND STAKEHOLDERS

- Ministry of Agriculture, Forest and Rural Development, PHARE PIU
- Ministry of Agriculture, Forest and Rural Development, Phytosanitary Direction and local branch offices
- Ministry of Finance, CFCU
- EC Delegation to Romania
- Contractor: SAVA Brunsbüttel (BRD)
- Supervisor: Ramboll (DK) in consortium with Tauw (NL) and Umweltbundesamt Austria, (A) with IHPA as Subconsultant
- Stakeholders: Ministries of Environment and Transport, local authorities.

SUPERVISION MANAGEMENT

Re-assessment of Inventory – Site Take-over

A re-assessment of the Inventory had to be made because the existing information was relatively old (from 2001-02). Local Phyto-sanitary Units enforces legislation and receives obsolete pesticides.

The re-assessment provides up-dated information for the Contractor's take-over of the site (logistics, contents).

The updated inventory gives a clear picture of the situation at take-over, and makes it possible for the Contractor to improve the planning and the supervision's cost control. The new inventory is managed by Waste Information Management (WIM) System (Tauw bv.).

The site take-over from Authority to Contractor (Site Take-over Document) requires:

- Agreement on re-assessed amounts
- Agreement on Contractor's liability
- Signature of parties involved:
  1. Legal representative of Ministry of Agriculture (local phyto-sanitary Director)
  2. Contractor (Site Manager)
  3. Supervision (Engineer)

The Contractor's clean-up operation requires

- Logbook
- Repackaging lists (based on weight)
- Weekly meetings with Supervision.

Repackaging, Weighing, Temporary storage

The project ensures:

- that the pesticide waste is repackaged in UN approved packaging materials, under strict occupational health and safety measures.
- an on-site laboratory for identification of waste composition
- transport according to ADR rules
- disposal at licensed incineration facility (SAVA in Brunsbüttel, Germany).

Site Hand-over

The site hand-over from Contractor to Authority/Owner (Hand-over document) requires:

- An agreement of repackaged amounts
- Back into Authority's liability
- Signature of parties involved:
  1. Legal representative of Ministry of Agriculture (local Phyto-sanitary Director)
  2. Contractor (Site Manager)
  3. Supervision (Engineer)

The Contractor's payment is based on Site Take-over and Hand-over forms (Euro/tonnes), and export lists.

LESSONS LEARNED

- Inventories should be re-assessed to have control of the project execution;
- Necessary to have local authority commitment and participation in facilitating works execution;
- Focused contract with definition of liabilities and responsibilities;
- Sufficient administrative backup necessary (contractor and supervisor);
- Quality-oriented Works Contractor is a must;
- No Project Management without field visits and hands-on experience;
- Flexibility and sensitivity towards work planning and external factors (e.g. weather, accessibility).

MANAGEMENT OF OBSOLETE STOCKS: THE INNOVATIVE OBSOLETE PESTICIDES MANAGEMENT PROGRAM WIM

Jan Betlem

Independent Consultant Obsolete Pesticides Management

WHAT IS WIM?

An inventory is the starting point and foundation of a workable clean-up plan with regards to obsolete pesticides. The scope of the problem has to be known before solutions can be developed (FAO Training Manual for Inventory taking of Obsolete Pesticides).

During the last decade, many countries have embarked on the detailed stocktaking of obsolete pesticides as a basis to formulate further actions. Although a standard FAO[1] form is widely promoted, one of the problems was, and still is in nearly all countries and organizations involved, that no computerised database is available in order to store the collected field data in a structured and retrievable way.

Developed and tested in the field and applied already in various countries, Tauw Group bv has recently improved its **Waste Information Management (WIM)** database: A Microsoft Access database application based on the standard FAO forms for Obsolete Pesticides Management from the start of the inventory up till the supervision and monitoring of the repackaging for disposal.

WHAT CAN WIM DO FOR YOU?

Once you have collected the inventory data in the field and the standard FAO formats for each site and each identified waste per site have been filled in, the fieldwork can be considered completed. However, you still have no overview and analysis of the data, like:

- What are the main wastes identified?
- How much waste has been recorded? Liquid, solidified, solid, other?
- What are the main manufacturers of the identified waste (important for potential co-funding)?
- Do we have a few large sites or many small sites and where are the sites situated (important for logistics at a later stage in the project)?
- Who are the legal owners of the observed wastes (important for legal ownership issues later in the project)?
- What is the condition of the observed packaging materials (can the waste be transported, how should it be re-packaged)?
- etc.

LOG IN

Users have to log in with a username and password. Each user is a member of a user group with specific user rights for tables, queries, forms etc.

The required language should be selected during the login. Currently, the main working screens (data input and data manipulation) of WIM are available in English, Spanish, French and Russian. More languages are expected to follow soon.

DATA INPUT

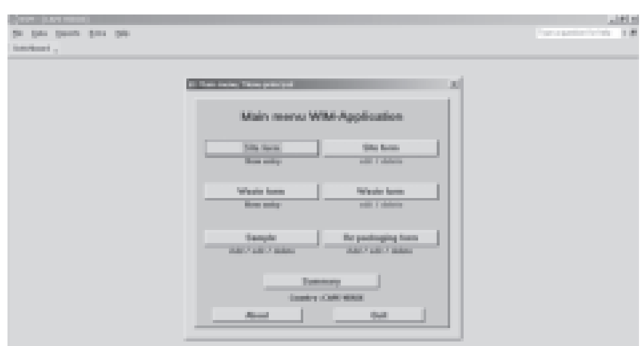
The program has several levels of **data input** according to the standard FAO inventory forms:

- Site information data (consisting of data about the respective site, such as environmental issues, ownership, condition of store, features of the store, etc);
- Waste information (consisting of data about the identified and un-identified wastes within one particular site, like trade name, name of active ingredient, quantity, package details, etc);
- Sample information (origin of the sample, but the outcome of the laboratory analysis can later be imported in this form as well).

New features of WIM include that at a later stage in the cleaning up project, data concerning re-packaging and transport to a central storage facility or even data related with the export to a final disposal facility can be included and re-called.

As such, the Project Manager has a perfect overview of all involved sites and quantities of wastes including the movements of the wastes up to and including the final destination.

With WIM, manipulation of quantities and fraudulent reporting (for example by involved contractors and/or transporters) can easily be detected and thus avoided.



WIM can deal with data of several types of waste. The application can be used for data input and analysis of other chemical wastes (industrial wastes for example) and veterinary waste as well.

DATA MANIPULATION

Once data has been entered, it can be **edited and deleted** afterwards.

[1] FAO: Food and Agriculture Organization of the United Nations.

Manufacturer	Active ingredient	Concentration		Site number			Form. Type	Total quantity		Trade name	P/V/I	Manufact.	Arrival
not relevant	not relevant			19	D	1	Powder	1000	kg	contaminated dust from floor	P		
not relevant	not relevant			20	A	3		8	m3	empty packaging material	P		
Pechiney Procil	Parathion			18	B	3	Liquid	2000	litre	Parathion	P		
Pechiney Procyl	parathion			20	A	9	Liquid	510	litre	Ethyl parathion	P		
Procida Groupe Roussel	BHC			19	A	6	Liquid	9000	litre	HCH	P		
Quino	Oxyquinoleine	140	gr/litre	21	A	15	Liquid	90	litre	Cryptonol	P		
Senchim	Dimethoate	400	gr/litre	21	A	8	Liquid	70	litre	Dimethoate	P	01-01-1992	
Senchim	Endosulphan	350	gr/litre	21	A	9	Liquid	104	litre	Thiosulphan 25 EC	P		
Shell Chemicals	Dieldrin			17	A	3	Solid	1250	kg	Dieldrin	P		
Shell Chemicals	Dieldrin			17	A	2	Liquid	1000	litre	Dieldrin	P		
Shell Chemicals	Dieldrin			17	A	1	Liquid	10000	litre	Dieldrin	P		
Shell Chemicals	Dieldrin			18	B	1	Liquid	9600	litre	Dieldrin	P		
Shell Chemicals	Dieldrin	5	%	19	A	1	Liquid	6500	litre	Dieldrin	P		01-01-1965
Shell Chemicals	Dieldrin			19	A	2	Liquid	6000	litre	Dieldrin	P		
Shell Chemicals	Dieldrin	25	%	19	A	7	Powder	1000	kg	Dieldrin	P		

All three levels are interconnected with each other. For example it is possible to switch from a specific waste to the site information and vice versa.

The searchable data base application can carry out all kinds of analysis and can present the outcome in tailor-made customer oriented tables. The outcome can be printed, or sent in digital form by e-mail.

For users in need of producing an inventory output according to the FAO format, WIM automatically prepares an Excel worksheet according to the general used FAO format.

A search function is available to search for specific information.

In order to obtain a quick overview, one option provides a summary of all data entered in the database.

THE LATEST DEVELOPMENTS OF THE WIM APPLICATION

WIM has recently been upgraded and a new version is now available for interested user-groups.

Specific extensions of the application concern the development of a “Repackaging and Export” module. This module allows supervisors during the repackaging and preparation for export to follow all steps related to repackaging, local transport to one or more central depot(s), international transport and export of the repacked obsolete pesticides.

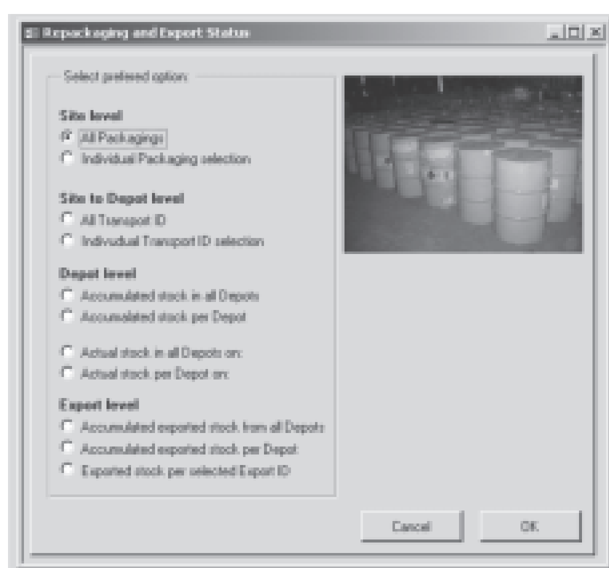
As such, statistic overviews can be presented allowing supervisors to monitor the cleaning up process.

WIM is currently the only available computerised database allowing user groups (such as governments) to follow and monitor the whole chain of activities from the early start of the inventory of obsolete pesticides in a country up till the very end of repackaging and export.

A special selection screen allows the user to get an immediate overview of relevant repackaging data on the ‘site-level’ and on the ‘central depot-level’. Detailed data can be generated related to local transport of repacked obsolete pesticides.

If the repacked obsolete pesticides are to be exported for disposal, a function is available for monitoring the international transport (for example per exported truck of sea container) and to monitor the total amount of exported repacked obsolete pesticides (important for example to follow the progress of and payment to an involved contractor).

So far, Government institutions in Tunisia, Thailand, Cape Verde, Senegal, Mauritania, Syria and many others have enjoyed the benefits brought by the application during the implementation of obsolete pesticides activities.



A fully operational GIS module has recently been attached to WIM in order to produce data in a GIS environment. As such, maps of the country or region involved can be shown, printed, or pasted in reports, displaying the position of (selected) sites with custom-defined features and details.

Future developments of WIM will preferably be made with international organisations and should be ‘server-based’ in order to allow access-for-all to the gained knowledge and experience.

WIM IS EASY TO HANDLE

Experience has shown that data can be entered into the WIM system during the fieldwork period. Immediately after fieldwork, the data analysis can be made visible and printed out.

WIM is not developed for scientific purposes. It is a practical tool to be used in the field and afterwards for the purpose of data analysis and the generation of overviews and specific reports.

WIM provides supervisory and monitoring tools for the various steps in an obsolete pesticides project, from inventory up to and including repackaging and export for disposal.

WIM provides standard format reports which can be used during Steering Committee meetings and presentations throughout the course of an obsolete pesticides disposal project.

WIM is innovative, time efficient and already implemented in several nation-wide inventories and cleanup projects worldwide.

WIM is a must for every organization dealing with obsolete pesticide management!

For further information concerning WIM, please contact Jan_Betlem@hotmail.com.

OBSOLETE PESTICIDE DISPOSAL PROJECT IN ETHIOPIA

Pasi Silvennoinen

Ekokem Ltd., Finland

INTRODUCTION

Obsolete pesticide disposal project in Ethiopia was carried out during the years 2001-2003. During this project 1500 tonnes of obsolete pesticides were collected and repackaged from over 220 different stores, centralised to 10 regional collection centres, shipped to Finland and disposed of by high temperature incineration at Ekokem Ltd’s facilities in Riihimäki, Finland.

Ekokem Ltd is a Finnish hazardous waste treatment company in Finland, which was established by the Finnish State, municipalities and industry in 1979. For filling its capacity, Ekokem has imported hazardous waste for high temperature since 1986 from over 30 different countries worldwide. Ekokem was contracted to carry out the project in Ethiopia after an international bidding competition.

The project was financed by the Netherlands, Sweden and USA through the Food and Agriculture Organization of the United Nations (FAO). FAO also arranged the international bidding competition. FAO’s Field Project Manager was managing all the preparatory work in Ethiopia before the disposal operation started, as well as the supervision of Ekokem’s performance during the disposal operation. The Ministry of Agriculture of Ethiopia (MoA) was the beneficiary of the project and the personnel from the MoA Plant Protection Department were involved in the management and supervision of the project.

SITE VISIT AND INVENTORIES

The project in Ethiopia was the biggest ever completed obsolete pesticide disposal project. For making this project successful, the importance of a good preparatory work was extremely high. The contractor site visit, which was arranged before the tender, was very well organised and gave a good picture of the local conditions in Ethiopia. The site visit lasted three weeks and it included a two weeks field trip, during which the suggested eight regional collection centres plus some of the most contaminated sites were visited.

Due to fact that Ethiopia is a big country, having area of over one million km^2, the distances are long. Road conditions are in most cases very difficult and especially during rainy season, June – September, many sites are inaccessible.

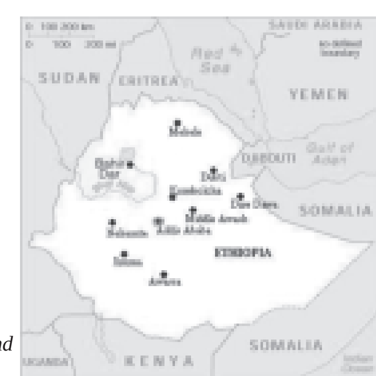


Figure 1: Map of Ethiopia and Collection Centres

Mountains and lack of good transportation equipment give also own challenges to the transportation. Because the site visit was carried out in the end of rain season (August – September 2000), it gave an excellent picture of the challenges, which could be faced in transportation.

MoA had completed a detailed inventory of the obsolete stocks. However, in some cases the inventories were not accurate, but still gave a helpful tool for planning the repackaging operation. MoA also had selected collection centres, which could be used for centralising the waste materials from small sites. This kind of preparatory work was extremely helpful in proposal preparation and finally in starting the implementation of the repackaging work itself.

PROJECT IMPLEMENTATION

Before starting the repackaging operation Ekokem arranged a two weeks training course for 25 persons from the MoA. The training included Occupational Safety & Health, IMDG and First Aid courses. Four of these 25 persons worked in the project management in close co-operation with Ekokem and FAO project managers. The rest of them worked as local counterparts in their own geographical regions. The assistance of the MoA regional personnel was necessary in successful completion of the repackaging operation. One of the major positive things during the project was MoA staff's commitment to the project.

During the project strict working standards were followed:

– All the local workers were trained accordingly to follow safe working methods.

– All the field activities were carried out under control of Ekokem's project supervisors and MoA's local counterparts.

– Personal protective equipment (PPE) was used accordingly.

– Paramedic/nurse was available at major working sites all the time.

– Cholinesterase tests were taken regularly from all the workers participating in the repackaging work.

– Task based risk assessments were done for each repackaging operation.

– The transportation and shipment was carried out according to international ADR and IMDG regulations.

– The licenses for pesticide waste shipments were applied according to Basel Convention and EU regulations.

– The incineration was completed according to strict EU standards in Finland.

All the equipment and materials, including PPEs, packaging materials, tools, machines etc., which were needed in the project, were imported to the country. Only some minor local material purchases were made. FAO provided vehicles for personnel transportation and one small truck for equipment and waste transportation. Locally hired trucks were used in local transportation.

When starting the project a new, updated inventory was completed and it was found out that the amount of 1500 tonnes

Figure 2: Pesticide store in Dire Dawa before and after operation

was almost doubled. However, the funding was not enough to complete the disposal of this bigger amount. This is why it was decided to concentrate on the pesticide stores, which posed the biggest threat to the environment and the people. This lead to the plan that the stores, which were in the poorest condition, had the biggest amounts of liquids and/or POPs pesticides and which were close to residential areas, were removed in the first phase. Finally 220 stores from 950 sites were cleaned up. Most of the small sites and the stores, which were in a good condition, were left behind.

Over 100 different pesticides were found from the country and almost 400 tonnes of the total 1500 tonnes were persistent organic pollutants (POPs). Seven POPs pesticides out of nine were: DDT, Aldrin, Dieldrin, Endrin, Chlordane, Heptachlor and Hexachlorobenzene.

CONCLUSIONS

The obsolete pesticide disposal project in Ethiopia was a pilot project to the Africa Stockpiles Programme, which aim is to clean up all the African countries from obsolete pesticides within the coming 15 years. Because local people was fully involved in the project at all stages, Ethiopia has now own capacity to carry out a major part of the ongoing second phase of the obsolete pesticide disposal project. Possibly this capacity can be used also in other countries, which face similar problems with obsolete pesticides. The project in Ethiopia was a good example about good preparatory work and co-operation between all parties at all stages.

IS SHIPMENT TO THE EU THE RIGHT APPROACH FOR OBSOLETE PESTICIDE DISPOSAL?

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ABSTRACT

This paper discusses the possibility of establishing a treatment facility for the Obsolete Pesticides (OP) locally, instead of transporting the OP to Europe for disposal, which has become the normal practice (FAO, EU and other donors).

NIRAS has in Mozambique assisted DANIDA, and in Senegal, Mauritania and Cape Verde the Netherlands Embassy in Dakar in advising the local governments regarding safe repackaging and shipment of 1,840 tonnes of OP for incineration in Europe.

In Latvia, Chemcontrol / Soil Recovery have installed a small incinerator for disposal of 1,800 tonnes of OP. The installation is operated in accordance with the requirements of EU Directive 2000/76/EC on incineration of waste. The experience from this project proves that OP can be disposed off at prices that are competitive with shipment to Europe (assuming that other types of waste are available for incineration after disposal of the OP).

The conclusion of this paper is that whenever OP projects are prepared it should be investigated which of the above mentioned approaches should be applied, especially taking into consideration a broader approach to the entire waste situation and hereby the sustainability of the chosen solution.

Shipment and disposal in Europe will solve the acute problem. However, it will not raise the environmental awareness of the local society nor provide a sustainable and long term solution in the same way as the establishment of a local facility will. A local disposal facility can also be used to treat other types of hazardous waste (HW) or Health Care Risk Waste (HCRW) for which there often is no solution.

Many companies are concerned about investing in countries without proper waste management, due to the danger of hampering the company's environmental reputation. The set-up of a local disposal facility will provide environmental correct disposal and may therefore contribute towards attracting foreign investments.

Key Words: Local Disposal, Export, Incineration, Obsolete Pesticides.

INTRODUCTION

Through the successful completion of a number of OP projects, the approach including repackaging and shipment of OP to the EU with subsequent disposal has become normal practice in FAO, EU and other donor projects involving OP disposal. The projects have mainly been undertaken in Africa but also Albania has shipped OP for disposal in Europe and last year Romania initiated a similar project. Therefore this approach must be expected also to be the preferred method for projects to be undertaken in EECCA countries which also stores large quantities of OP (Ukraine 19,300 tonnes; Moldova 6,600 tonnes; Bulgaria 5,333 tonnes and Kazakhstan 1,560 tonnes)[1] unofficial data indicate 12,000 tonnes OP in Bulgaria.

The approach is well conceived due to the fact that proper local disposal facilities that can comply with the EU treatment and emission standards are non existent in the affected countries. Additionally, the approach considers all phases of the disposal operation and applies facilities in the EU which meet the EU requirements and additionally provide operational experience, hereby guaranteeing the environmentally correct disposal. It may, however, be considered if another and more visionary approach, considering the establishment of a local disposal facility, could be adapted.

Below, the experience from projects applying the repackaging and shipment to the EU approach as well as the findings from the establishment of a local treatment facility is described.

The intention of this document is not to brush aside the well-established system, but merely to highlight and bring to the attention of the countries and donors that there might be a different and more comprehensive approach which, in certain countries, would be feasible and sustainable and at the same time provide a broader solution to HW management, including OP.

METHODS

Shipment and Disposal in Europe

Mozambique

In Mozambique, the Danish Government through their DANIDA programme supported the authorities in collection and disposal of OP and OP contaminated soil. In total, 1,075 tonnes of OP and contaminated soil were collected from 11 locations during 2000-2002.

The intention was to dispose a small amount at a local cement factory. However, local resistance, backed by a NGO, halted the disposal and the OP was finally sent to Europe for disposal at a high temperature incineration installation.

Senegal, Mauritania and Cape Verde

In Senegal, Mauritania and Cape Verde[2)] the Royal Netherlands Embassy in Dakar supported the authorities in collection and disposal of OP. In total, 786 tonnes of OP were collected from 45 locations throughout 2002-2004.


Picture 1 and 2: Storage and repackaging of OP in Senegal

The disposal of the collected OP was carried out in Europe at high temperature incineration installations which comply with present EU regulations.

Romania

In 2004, the CFCU on behalf of the Ministry of Agriculture, Forests, Waters and Environment in Romania awarded a contract for collection, shipment and disposal of estimated 1,409 tonnes of OP located at 133 storages throughout the country[3)]. In connection with the collection and disposal operation, the Ministry hired a consultant to supervise the operations and provide Technical Assistance (TA) to the Ministry.

The disposal will be carried out in Germany at a high temperature incineration installation.

Ethiopia

During 2001-2003, FAO supported the collection and incineration of OP from the entire country[4)]. In total, a quantity of 1,500 tonnes were collected and shipped to Finland for disposal.

Bulgaria

During 1999-2000, the Dutch Ministry supported a study on collection and incineration of OP[5)]. Subsequently, a quantity of 30 tonnes in total was collected and shipped to the Netherlands for disposal.

Disposal at Local Treatment Facility

Latvia

In Latvia, Chemcontrol in the beginning of the 1990s provided training in repackaging of OP and supervised the initial repackaging. During the following years the trained team repacked 1,800 tonnes of OP from a number of local storages and transported them to 2 upgraded storages.

Picture 3: The site for disposal of Obsolete Pesticides in Latvia.
The incinerator is located in the building at the back.

The Ministry of the Environment in 2000 investigated the possibility of shipping the OP to Finland or Denmark for disposal. However, the MoE realised that it would be better to establish a local facility which also could cater for HW which was an emerging problem. Originally the intention was to provide the service to all the Baltic States but this proved not to be possible and therefore the MoE decided to establish their own installation.

In 2003, Chemcontrol / Soil Recovery (Denmark) supplied a modified CIS 2500 incinerator system for the disposal of the stored OP[6)]. When the stored OP has been disposed of, the installation will be used for disposal of other HW.

Disposal

The CIS 2500 incinerator system is designed for incineration of solid and liquid HW. For the project in Latvia, the system was modified to accommodate the high chlorine and sulphur concentrations.

Picture 4: Two CIS 2500 units in operation in Malaysia

The incinerator is a turn-key installation consisting of two standard 40 ft. containers and one 20 ft. container fully fitted in Denmark, requiring limited on-site installation. The container-based concept makes it possible to move the installation from one site to another, if so required. The installation includes all systems required for safe operating and is in full compliance with the demands specified EU Directive 2000/76/EC on incineration of HW. The capacity of the plant is 2,000 - 4,000 tonnes per year, depending on the waste composition and especially the calorific value of the waste.

The system operates at a temperature 1,100 °C and the flue-gas cleaning system guarantees compliance with the emission specified in the EU directive. The composition of the emitted gas is registered by the continuous air monitoring system providing on-line measurements of NO_2, HCl, TOC, CO_2; SO_2 and dust.

RESULT AND DISCUSSION

Shipment and Disposal in Europe

Experience shows that the approach of shipping the OP to Europe for disposal has been very successful. From a donor point of view the procedures involved now has been applied on a number of projects and therefore provides a certain guarantee that the projects are completed successfully.

Problems Encountered

In connection with the shipment to Europe only a few problems were encountered, mainly:

- The coordination and project management in many cases are more demanding than anticipated.
- Problems related to custom clearance of equipment and packaging material.
- Odour during transportation

None of the problems caused major obstacles to the implementation of the projects.

Economical Aspects

Experience from the two projects managed by NIRAS shows that the disposal cost and TA including check of inventory, tender documents and evaluation, supervision and disposal amount to approximately 2,800 Euro/tonne.

In Romania, the total cost for both components is 3,888,000 Euro or 2,760 Euro/tonne. The cost for preparing the tenders documents and tender evaluation has not been included in this amount as it has been undertaken by the Ministry and the EU representation to Romania.

In Ethiopia, the total cost was 4,750,000 US$ equal to approximately 3,170 ˆ/tonne.

The total cost for disposal of the OP in Bulgaria were 95,000 Euro equal to 3,170 Euro/tonne.

In case all phases of the project are considered a total cost of approximately 3,000 ˆ/tonne of OP is considered realistic. The main expenditure of the projects concerns the collection and repackaging operations which largely depend on local salaries. Based on previous experience it has been found that the funding provided for OP projects typically are spent as follows:

– Repackaging 55%
– Transport 15%
– Disposal 20%
– TA 10%.

Disposal at Local Treatment Facility

The amounts of OP handled by the donor projects are often small and do not by itself justify the establishment of a local disposal facility. However, most developing countries have some basic industry which generates HW. This waste is at present without any doubt disposed of in an uncontrolled and environmentally unfriendly manner. By establishing a disposal facility, the Government will be in a position to provide a proper disposal solution to the industry and, equally important, start enforcing proper waste management.

Problems Encountered

In many countries, there is opposition against incineration, mainly due to fear of being exposed to the components emitted from the process, especially dioxin. The opposition is typically very emotional and despite of provided proof from similar installations and guaranties that the installation is capable of complying with all requirements given in the EU incineration directive, meaning that the installation should not pose a threat to the local citizens, the opposition remains strong. In Latvia, the facility also experienced this opposition. The opposition came very late in the project.

Economic Aspects

The cost of the incineration system is roughly 2,400,000 Euro. In Latvia, 50% was provided as a grant from the Danish Government and the remaining was provided by Latvia through the Ministry of Economy.

Besides the incinerator foundations, a building to protect the equipment from the harsh weather conditions was constructed. In addition to the hardware cost, additional expenses for preparation of EIA and TA have been encountered.

The operational cost, including disposal of the slag and filter cake from the flue-gas cleaning, shall be added to the investment. Experience shows that this amounts to 0.15 – 0.2 Euro/kg OP. When disposing of normal HW the cost will be lower.

DISCUSSION

Although the "shipment and disposal in Europe" approach solves the acute OP problem in a proven and well established way, it provides very little changes to the overall capability of the country in question with respect to solving environmental problems, just as it does not contribute to raising the environmental awareness of the local society, nor provides a sustainable and long term environmental solution. Especially in EECCA countries it must be expected that the industry will develop rapidly, resulting in increased amounts of HW. This makes the demand for proper disposal facilities even more obvious.

The establishment of a local disposal facility will facilitate these aspects and may additionally also provide a solution to other types of HW or HCRW for which there in many cases is no solution.

A project concerning the construction of a local disposal facility does not require larger financial support from the donor organisations than a project shipping the OP to the EU. However, to justify a local disposal facility it is imperative that the local industry produces a certain amount of HW which requires disposal by incineration and that the waste generators are capable of paying the fee charged for the service.

The benefits are the disposal of HW, development of the capabilities of the local administration, instead of bringing in international experts for a short period. Further, it will allow the country the possibility to implement proper waste management systems, and allow the Government of the country to implement and, just as importantly, to enforce regulations on HW.

In order to provide an estimate on the financial consequences of a project, including disposal at a local facility, a case study has been prepared. The study assumes that 1,500 tonnes of OP will be disposed of during the first 3 years of operation and that a total of 36,000 tonnes of HW will be disposed of during the expected 15 year lifetime of the installation.

Besides the investment in the equipment and supporting facilities, it will still be necessary to allocate funding for repackaging and transport. It should however be possible to

Table 1: Financial Data used in Scenario

			LOCAL DI SPOSAL		SHIPMENT EU
Amount of OP	tonne		1,500		1,500
Repackaging	€		2,025,000		2,475,000
Transport	€		450,000		675,000
TA / Supervision	€		450,000		450,000
Diposal	€		N.A		900,000
	€		2,925,000		
Available for disposal (Grant)	€		1,575,000		
Grand Total	€		4,500,000		4,500,000
Calculation of Treatment Fee to be Paid by Industry					
Years of operation			15		
Other waste	tonne		36,000		
Investment (equipment, site, test, training)			3,300,00 0	€	
TA and operational assistance			700,000	€	
Grant	39%		1,575,000	€	
Loan	5% p.a		2,425,000	€	
Dept service			3,504,451	€	
Operation cost			3,150,000	€	
Salary (10 staff)			3,000,000	€	
Maintenanc e (% of total investment)		4%	1,980,000	€	
Total Expenses			11,634,451	€	
Income	€/tonne	325	11,700,325	€	

reduce these costs slightly, since it will be possible to reuse the repackaging material and since the number of trained staff required for repackaging operations will be less due to the fact that a longer time frame (1 to 2 years depending on the amount) can be accepted, and actually is preferable as it allows for preparation of a better waste feed mixture to the incinerator system. The extended time frame will also allow for better logistics. A reduction of 10 % is assumed. As only local transport will be required it is expected to be possible to reduce the cost by 5%. TA is considered to be the same.

Table 1 presents a comparison between the figures mentioned above for a project where the OP are shipped to EU for disposal and disposal at a local installation. Based on the above assumptions on reducing the cost for repackaging and transport and the typical overall cost of 3,000 Euro/tonne of disposing the OP, the amount available to be given as a grant would be 1,575,000 Euro.

Using this amount as a grant, Table 1 calculates the disposal cost to 325 Euro/tonne of HW supplied by the industry. This is less than what is typically paid in EU countries. In case the industry is able to pay more than this amount, the grant required may be reduced making it cheaper than export to EU. However, the visionary concept would be that the donors considered a larger grant hereby making it even more affordable for the industry to hand over their HW for disposal and in this way assisting the system in the early and difficult stage. A 75% grant would for example result in a treatment fee of only 270 Euro/tonnes.

ACKNOWLEDGEMENTS

The author would like to express his gratitude to Soil Recovery for access to their operational data from Latvia, and to Mr. Preben Røgild Knudsen from NIRAS for details on the projects related to collection, shipment and disposal of OP.

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PESTICIDES AND INSURANCE, A CHALLENGE FOR RISK LIMITATION IN PROCESSING, MANAGEMENT, SAFEGUARDING AND DESTRUCTION OF PESTICIDES

Reiner Schuette

- Why is insurance required at all in pesticide use and processing?
- What types of insurance are required here?
- Is liability insurance sufficient under certain circumstances for overall coverage of this risk?
- Who does this insurance apply to?

Storage, transfer to another site, disposal, destruction and transport for all those involved – all pose a risk potential which requires attention to risk limitation.

In particular, the pesticide management of old decrepit pesticide stores poses an extensive risk for authorities, operators, estate owners, operator companies and treatment firms.

Insurance protection in all fields of obsolete pesticide management is of great importance.

One must also take account of the specific risk structure of pesticide destruction, pesticide transport and safeguarding of pesticides.

There is fundamentally no universally applicable solution, since each case of individual processing is different.

In addition to the risks of storage, obsolete pesticides cause the risk of uncontrollable processing, since to some extent pesticides of unknown origin are found in the storages.

Added to this, one has to take the authorities into consideration, who - in addition to the necessary proof - also have different approaches to the possibilities of pesticide destruction and long-term storage.

BASIC PRINCIPLES OF LIABILITY INSURANCE

Liability insurance fulfils the requirement of exoneration from or financial coverage of liability claims that may specifically arise in the field of pesticide processing.

Dealing with such claims requires a large amount of energy as well as resources, time, personal commitment, juristic know-how and money, let alone the juristic and legal background knowledge required in the case of a dispute.

Ultimately, the cash value fulfilment of the claims also still remains in case of recognised liability.

Legal liability is the legal obligation to take responsibility for damage caused.

This means that the responsibility for such damage is not arbitrary and the laws of a land must be defined when one speaks of being held liable.

These laws are also known as liability norms, since there cannot be any liability without a norm that defines that one is rendered liable.

A person who suffers damage must be able to refer to a certain liability norm in order to assert his/her compensation claims against the damager.

These norms also lay down the prerequisites that must be fulfilled for liability to exist at all.

One may also, however, become liable to pay compensation on the basis of a contract.

The contractual parties are free, as part of a contract negotiation, to oblige themselves contractually to recoupment and exclude legal liabilities that are non-compelling within the framework of the legal possibilities.

However, caution is called for here!

Liabilities over and beyond the legal liability are in principle not covered by the insurance contract.

Special agreements are required in this case, to be observed specifically in the field of pesticide destruction and processing.

In the sense of risk management, it is therefore to be regarded as critical if disadvantageous liability clauses are agreed in the contracts between partners.

One must clearly differentiate between legal liability and proper fulfilment of the contract.

Naturally, clients are obliged to keep their contractual agreements.

If, therefore, a company fails to provide the service that was ordered during the pesticide negotiations, the obligation arises according to contractual law to make good or repair the service.

This does not in principle have anything to do with liability and liability insurance.

Therefore, the costs of making good the service that was not correctly provided can never be borne by the liability insurance.

In general insurance law, one must distinguish between the types of liability insurances involved.

We are essentially concerned here with all the types of liability coverage that have to do with the risk structure of destruction, transfer to another site, transport and storage of obsolete pesticides.

Therefore, in this case liability risks are covered for all companies and individuals dealing in some way with processing of pesticides (company operators, industrial companies, freelancers, artisans, workers, owners, communities etc).

WHO IS INSURED?

Insurance coverage extends to persons who come to deal with pesticides in some way or another, in addition to the companies and the sponsorship that has assumed the currently required responsibility here for obsolete pesticides.

These include all other members of the company and workers who deal with the matter in the exercise of their professional activity for the employee, but also outside the business activity, e.g. security staff.

With coverage of the liability risks for workers, the exemption claim under labour law is simultaneously taken into account.

The important element in the formulation of an insurance contract is that if several pesticide processing firms, companies or organisations are involved, the latter also agree among themselves on insurance coverage which is not included in the normal liability coverage.

Switzerland, for example, has very specific regulations in this case that automatically include insurance coverage for claims of those jointly insured among each other.

In case of an occupational accident, the statutory accident insurance compensates for the damage to the employee and the liability claims against the employer or colleague who caused the damage are settled by the accident insurance.

For industrial subcontractors, the insurers regularly limit themselves to their service obligation with the liability of the own insured as the businessman making responsibilities possible and expressly exclude the personal liability of the subcontractor.

The latter is supposed to take out own insurance.

The services of the insurance can therefore be individually tailored such that there is an important prerequisite precisely in the processing of obsolete pesticide deposits.

The insurance protection encompasses, as does the liability insurance in general, the exemption of the insured from justified claims for compensation from third parties.

Furthermore, the insurance protection encompasses verification of whether and to what extent these claims are justified, in addition to fending off unjustified claims.

In this respect, the liability insurance is a passive insurance for legal costs that checks the costs of the verification and the legal protection, independently of the agreed insured sum of the insurer.

This, however, only applies to claims directed towards compensation for damage.

It does not apply to those directed towards fulfilment of contractual obligations or which deal with other aims, such as for example information, or the omission of certain actions.

The insurer usually pays compensation to the damaged claimant, i.e. generally to the insured.

Which risks are now insurable?

In liability insurance, the principle of the speciality applies.

Only the characteristics and legal situations that the insured indicates on signing the contract are fully under the insurance protection.

This is of particular significance in the insurance of obsolete pesticide deposits, since definite references to the signing of the contract and the risks not perceived at the time of signature result from the usual policies and the operating descriptions that they contain, so that these risks could under certain circumstances be charged to the insured.

In this case, the so-called precautionary insurance in the insurance policy is a clause that urgently needs to be agreed upon, which also covers the risks that the insured forgot to state at the time of signing the contract.

An internal correct shaping of the responsibility for this risk is therefore absolutely essential.

Individuals in the insurance sector often do not have the specialist knowledge required in the processing of obsolete pesticide deposits, to be able to envisage all risks that may emerge from this storage and processing.

It is absolutely essential in this case that the risk management team of such a pesticide storage deposit draws up a possible damage scenario and conducts a risk potential assessment.

As a rule, the insurer has formulated exclusions.

This applies to the entire area of liability insurance and the systems of conditions established, which are known as general liability conditions.

In addition, there are special conditions that may alter further areas of these general liability conditions and can usually be formulated in favour of the insured.

Therefore, for all customers the clauses agreed concerning damages occurring abroad or agreed supranationally must be included separately.

The regulation concerning activity-related damages, i.e. damages that stem from the activity itself, must also be amended when the processing of obsolete pesticides is involved in this case.

The individual stages of production, use, transport, storage and the handling of pesticides are not sufficiently covered with usually agreements concerning quality assurance.

Monitoring, controls of reception by the purchaser and also the supplier's liabilities are particular specialities here that constitute important prerequisites for liability insurance coverage during processing of obsolete pesticides.

However, liability undertakings that are above the law can also be safeguarded.

Anyone dealing in the field of obsolete pesticide processing can provide professional information on their risks and safety.

It is important in this case that in addition to the insurers, those given power of attorney for management are also adequately supplied with a risk catalogue.

A highly specific form of risk coverage is the occurrence of personal injury and material damages, which may in addition cause further damage to capital that is not covered by normal liability insurance.

Such damages can be additionally agreed upon in the further insurance protection.

LIMITATIONS OF LIABILITY

In many modern capitalist states, it has been usual for many years to limit the liability of the company or the investor.

In Europe, this was not the case in relatively early forms of enterprise and the entrepreneur had unlimited liability with his own private capital.

This was modified, however, approximately in the course of the industrial revolution, since a separation between the entrepreneur and the investor was introduced.

It was a completely incomprehensible situation for the entrepreneurs of the older generation at that time that the entrepreneur should not supply the complete capital himself, but also allowed shares from other investors or foreign ownership.

In particular, the participation of workers in the company by the issue of shares was specified by them.

With the limitation of liability to the amount of the capital employed, it was subsequently more readily possible to sell shares of companies, since these shares now no longer constituted any risk, but only potential profit.

This is certainly a reason why it was possible to sell the smallest shares to workers of the company at all.

A side effect was, however, that larger shares remained limited in liability too.

Limitation of liability was already heavily criticised by Karl Marx, since it allowed privatisation of the profits, and likewise the risks of the shareholders.

If the company was successful, the shareholders benefited. If however the company causes damages, the shareholders can no longer be obliged to pay compensation owing to the limitation of liability. Others are left with the damages in this case.

In this manner, according to Marx, the investors would evade their responsibilities.

Even today, there are still isolated bankers with full liability and full liability is still widespread among freelancers.

In the case of pesticides, it is therefore an unreasonable request on the part of the companies involved to consider possible liability limitations.

These liability limitations are subsequently arranged in the contractual negotiations in such a way that liability is minimised and so that the company rules out general potentials for liability.

Since this is not however in the interests of extensive processing of pesticides, liability insurance may be used in this case, reducing the so-called liability risk in the case of damages.

This is a risk, the calculated prognosis of possible damages, or a loss in the negative case of the hazard.

A risk can therefore also be defined as the threat to a person's values owing to natural events or human acts.

Concepts of value are, as is well known, very different and risk situations are therefore also to be viewed very differently.

What is a loss for one person under certain circumstances means a gain for another.

A risk is the probability of the occurrence of a negative event, which is multiplied mathematically or in the probability of the occurrence of a negative event with the financial extent.

It is therefore possible to avoid risks by either covering the entire consortium or individually involved companies within the context of the insurance policy by taking out a liability insurance including all possible risks.

The so-called risk management is a tried and trusted medium here for minimising risks by insurance, if observance of safety measures, material characteristics, maximum speed, protection of resources and environmental protection stipulated by protection of health and safety standards at work do not minimise any risk of a loss.

Risk management is therefore one of the most important means in order to be able to take out a policy in this case.

LEVERAGING LIMITED RESOURCES TO ACHIEVE MAXIMUM COLLECTION OF OBSOLETE PESTICIDES AND OTHER PROBLEM WASTES IN NEW YORK STATE

ROBERT L. (ROB) DENNY

ARROWCHASE, INC. ENVIRONMENTAL PROJECT MANAGERS

It is true that any discussion of the quantities of obsolete pesticide stocks in the United States pales in comparison to the mammoth challenges that often are presented at this 8th International HCH and Pesticides Forum and other similar events. The reason for this disparity in the "need" for stewardship may not result from any ongoing environmental commitment, but simple long-term economics. Pesticides have traditionally been more expensive in the United States and arguably, since at least the 1970's, somewhat more regulated than some parts of the planet. But the most significant reason, may be that, with few exceptions, governmental support for the purchase of pesticides has been rare, resulting in no instances of holdings of pesticides, in one location, measuring in the thousands or even hundreds of tons of product. Yet, although the problems may be smaller, pesticide stewardship challenges certainly do exist in the US, and the decisions that any entity must face in that disposal is virtually the same for any project manager anywhere in the world.

In the United States, neither the federal government nor that nation's pesticide industry assumes a significant responsibility in the recovery of obsolete stocks. The US Environmental Protection Agency has provided grants to States and smaller units of government in support of programs that have recovered obsolete stocks of pesticides, but there is no unified, consistent funding for this activity. The US pesticide producers, formulators and distributors often assert that their industry supports State programs through registration fees filed on each and every product registered for use, and hence sale. in an individual State governing body. In reality, though, the US industry provides markedly less support than many western countries and particularly less than the US neighbor to the north: Canada. Figure 1 hints of something of the irregularity in chemical stewardship in America, where a pesticide user's ability to practice environmentally sound disposal for unwanted, unusable or otherwise obsolete pesticides is largely a function of one's geography.

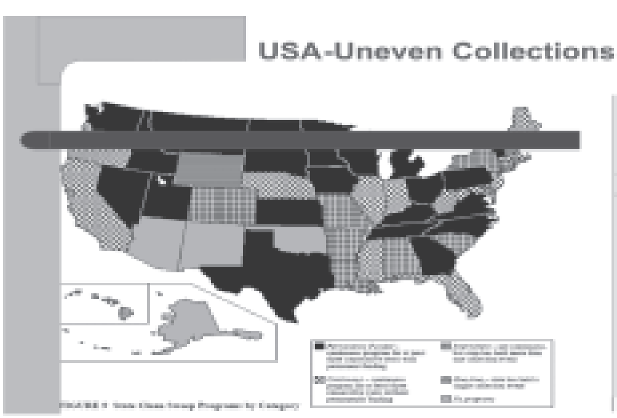


Figure 1: State Clean Sweep Program by Category

In late 2001, just after the tragic events of September 11th of that year, the State of New York was, indeed, one such under served geography in terms of the ability to dispose of obsolete stocks of pesticides. In light of the financial hit on that state's treasury, after 9/11, it appeared that there would not be any available funding for either programs or personnel to manage new programs for some time to come. Historically, unlike many agricultural states, there had never been a statewide effort for pesticide collection and destruction in New York . Yet, there were clear suggestions that a rather backlog of pent up demand for destruction did, indeed, exist. There had been, and in 2001 there still were, some limited federal grants to local governments supporting collections of pesticides. In recent years, even these very small grants have disappeared. It was in this climate, that determined management within the NYS Dept. of Environmental Conservation saw an opportunity to leverage ephemeral enforcement money and establish a finite program that maximized the obsolete stocks destruction while minimizing both the environmental and financial risks to the State. The author of this presentation was hired to work with that State management to effectively implement this stewardship task.

In early 2002, the basic "choices" that affected the public and private managers were outlined and weighed in their impact and their risks, including human, environmental and economic. From the very beginning all involved agreed that certain, so called decisions, were not on the table for discussion. For instance, it was never considered that this effort would involve a period of "study, evaluation, or inventory". The managers were relatively certain that some degree of demand for service existed and through our collective experience, we had a good idea of the types of products that we were likely to find, or, we knew we could adapt to any challenges that developed. Additionally, the mangers never considered burying or landfilling any product. The recovered materials were, from the outset, destined for high-temperature destruction OR recycling. The other theoretically potential decisions that was not considered was any form of exporting the problem outside of the jurisdiction of the US. The managers felt comfortable in the oversight provided by the US EPA and other State environmental authorities, and although few destruction facilities existed within the boundaries of New York, there were assurances that there were and are facilities in the US capable of safely disposing of obsolete pesticides.

The real decisions can be found summarized in Figure 2. The first two choices are inter-related. In the US, as in other countries, two types of collection events exist, and both have their strong, adamant proponents and detractors. One is the set, centralized event where materials are brought into a pre-designated location on a date certain and the products

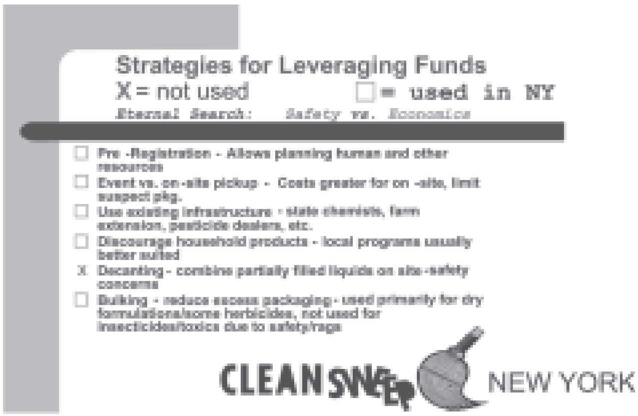


Figure 2: Strategies for Leveraging Funds

are classified, processed there for transhipment. This is the most common type of event for household hazardous wastes in the US. Another type of event is the on-site collection. This type of event involves the hazardous waste team going to the home, farm, or place of business of the holder of the pesticide and processing the pesticide for shipment "on-site". Obviously, the organizers of an on-site event must have advance knowledge of the pesticides and advance registration is assumed.

CleanSweep NY as the New York obsolete pesticides program came to be called, recognized that the on-site program could be the safest approach, involving less handling and exposure of pesticides; yet in many instances this expense was not warranted. Many pesticides had relatively new, intact packaging and could be safely transported to a centralized site. On-site collections are the most expensive collection method and CleanSweep NY reserved this approach for the most suspect packaging. Yet, open centralized collections, like those used by local governments for domestic hazardous waste can be impossible to predict in their size and expense if anyone is allowed to show up. CleanSweep NY determined that advance registrations, for both on-site and central events, would meter the appropriate amount of personnel and materials to each event, thereby avoiding both waste and overwhelming response with inadequate resources.

Another important decision not only saved the State of New York funds, but also left the earmarked funding more for actual destruction of pesticides vs. other services. That decision was concerning how much preparation and implementation should be outsourced. Over time, CleanSweep NY stuck a balance in the public-private management and even clerical support of the program. Yet, significant savings were also made by utilizing enforcement personnel to pre-screen holders that may/may not be holding products with suspect packaging that could not withstand shipment, OR to screen for unknowns that needed analysis. If analyses were warranted, the State chemistry personnel were utilized for sampling and characterization for Dept. of Transportation requirements. Constant examination and awareness maximized the funds available for actual chemical destruction.

The original foundation for CleanSweep NY was for agricultural pesticides that had been earmarked for use by either private farmers or the commercial applicators that served that same customer base. The general public or "homeowners" were never considered as candidates for this CleanSweep NY service. Yet, not long after beginning the CleanSweep NY program in the most sensitive ecological area of New York, called Long Island, the managers of the program realized that a large constituency of potential holders could not be labeled as "agricultural". In fact, on that sandy ecology and shallow surface area of Long Island, there were not only some farming remaining but also an almost equal weight of pesticide use from landscape gardening, arborists, park/recreation/cemetery vegetative management, and even marinas coping with the changing requirements of anti-fouling coatings for boats. Once this decision was made, an awareness and pressure grew to provide service to agricultural and food storage facilities that had elemental mercury on-site. Empty, properly rinsed metal and plastic pesticide containers were also a pressing need for recycling in some areas. And most recently, the CleanSweep program has allowed access in local, particularly rural school districts who do not have access to reasonably priced hazardous waste destruction for school laboratory chemicals and other hazardous wastes in the school systems.

Another decisions that was made relatively easily, was that the management of CleanSweep NY never really considered any consolidation techniques at either a centralized collection or on-site event that might increase the risk to either the State, the management, the hazardous waste contractors or the site owners. CleanSweep NY authorizes overpacking of products to maximize the materials under the same manifest number, but neither fuel blending, gas bubbling, nor decanting is allowed. Originally, CleanSweep NY took back some of the obsolete refillable mini-bulk tanks that are increasingly prevalent in the US, but now have been around long enough to earn the label: obsolete. CleanSweep quickly realized that paying hazardous waste prices for mildly contaminated plastics was not a good use of resources and we have a database of free or lower cost alternative industry collection programs available for this class of holder. In the beginning of the program, also attempted to recycle and reuse pesticide products that were virtually new and were still legal for use. In the end, the regulatory pitfalls potentially complicating that form of recycling were so immense that the time, and hence billable hours, were not worth the benefit. True "reuse" has not been attempted since.

One decision that was not made in the very beginning, but quickly evolved was in the realm of "cost sharing." As mentioned earlier, the original money was authorized for agricultural pesticides. It was, therefore, governmentally required that services extended outside of the agricultural community must, therefore, be on a different footing than holders within that farm base. Consequently, CleanSweep NY decided to charge, on a par with the low contracted rate for hazardous waste services, for holders outside of this community. It was decided at the outset to record the weights of products by holder, even for agriculture. And CleanSweep NY also realized that the process of both weighing in and settling payment for scores, if not hundreds of holders of sometimes small amounts of product could quickly turn into a bureaucratic nightmare. Therefore, non-agricultural hold-

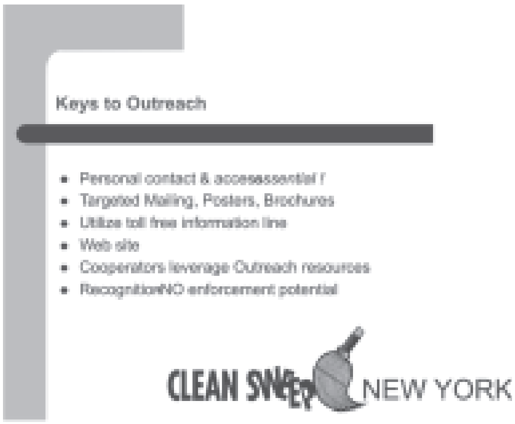


Figure 3: Identify Additional Cooperators

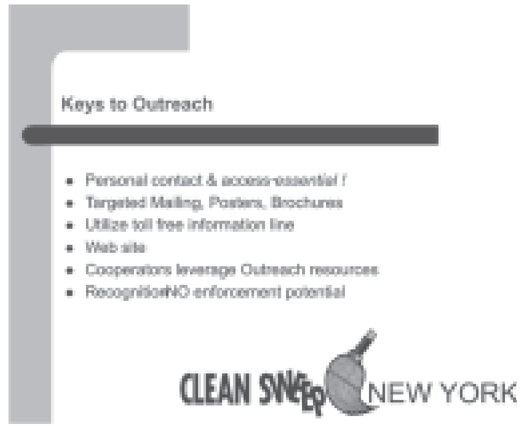


Figure 4: Keys to Outreach

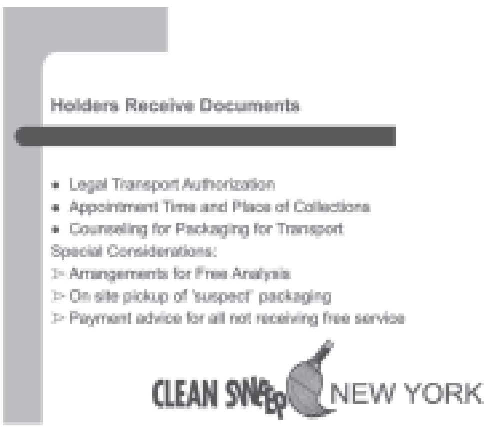


Figure 5: Holders Receive Documents

Figure 6: Provisions for On-Site Pickup

ers of pesticides, mercury, and certainly school chemicals and other government agencies were charged the contractor's rate/weight, but only after a quantity of product in excess of 100 lbs. (45.5 kg.) was submitted. The State paid for these smaller quantities and the process moved quickly, particularly when pre-registered holders were pre-identified as needing to pay and therefore were staggered in their appointment times, providing smooth traffic control and efficacy to any collection site event. Please note that neither the recycling of the metal or the plastic, properly rinsed drums and other containers has required either cost sharing or substantive State funding, to date, due to either industry support or the current pricing of the recovered commodity.

One key to any successful program is the dissemination of information into the hands of the holders of obsolete pesticides. If the holder does not know of, or appreciate the value of, the service provided then the collection will be less than its potential. CleanSweep NY operates at its best when the public and the private sector work together to reach pesticide holders. It takes local knowledge of the community to effectively target those holders and CleanSweep is usually effective in that outreach (Figures 3 and 4). Additionally, CleanSweep also utilizes a toll free information line, a web site and other communication techniques depending on the community and audience.

The net effect of this conscious pre-planning and evolved strategy is a US collection program that continues to remove obsolete pesticides from a mixed agricultural and specialty chemical population. By targeting a region at a time, the New York program does not just go where it is likely to garner the most return, but instead makes a political decision to cover the entire state, approximately the size of Bulgaria, in approximately 5 years. It is important to note that the largest amounts of obsolete stocks have been collected in New York City and the surrounding 100 km radius. Presumably, once the entire state is covered, the program will then proceed back to the eastern most point, Long Island, and begin again. But whether the program targets rural New York or more exurban environments, participants are either met at an on-site collection or show up at collection events, well prepared, informed of what is expected of them, cognizant of any cost sharing expected, and with rare exceptions move quickly through the process at sites selected for all weather operations. This is despite the fact that all collection events are scheduled pre- and post- harvest or, in other words, at a time when cold weather could cause problems in this part of the world. Yet, CleanSweep NY is designed for maximum participation, and those persons who make their living through farming or vegetative management are more likely to participate when the collection is not competing with their livelihood (Figure 5-9)

In the eastern US and even in the US as a whole, the CleanSweep NY is considered one of the better operated, most cost effective programs. This efficacy is in large part due to conscious persistent decision making and evaluation

Figure 7: The Collection Event

Figure 8: The Collection Event

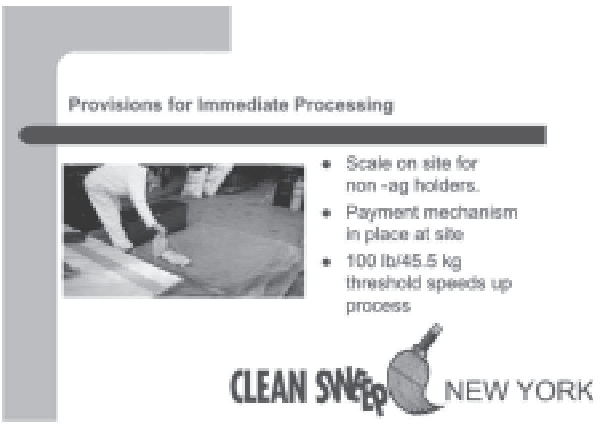


Figure 9: Provisions for Immediate Processing

of economics while managing risks at an acceptable level. This evaluation has much commonality to almost any obsolete stocks program. In a different environment or set of conditions, there will be a different outcome, but the range of decisions will likely be the same. Importantly, the New York program has accomplished this measure of success, without a long time-table for implementation, precisely because management went ahead and considered the breadth of their options. And although today's CleanSweep NY looks somewhat different than the one in 2002, it is still a fact that significant quantities of stocks were collected and destroyed in less than 6 months from initiation of this program, and within a very short while the structure fit the environment, policies, and economics while removing those quantities of obsolete pesticides.

LESSONS LEARNED DURING A PROJECT TO DISPOSE OF OBSOLETE PESTICIDE STOCKS IN WEST AFRICA

C. D. WALLER, L. DOLLIMORE

Crop Life International, Belgium

INTRODUCTION

The West Africa Obsolete Stocks project completed in 2004 was a Euro 2.4 million initiative that resulted in the collection and disposal of 786 tonnes of obsolete pesticide stocks and associated waste by high temperature incineration in Europe. It was particularly interesting because:

1. It was a combined 3-country project, covering Cape Verde, Mauritania and Senegal.
2. It was a public/private partnership initiative, involving not only the national governments, but also the Netherlands Embassy in Dakar, CropLife International and seven original manufacturers of some of the stocks.

The Netherlands Embassy was the project sponsor and contracted consultants to coordinate and monitor the project on its behalf. The operational work was contracted to SAVA GmbH, the German hazardous waste management company, based on an international tender. SAVA subcontracted the field work to Tredi S.A., the French hazardous waste company.

The Governments of Senegal, Mauritania and Cape Verde had the overall responsibility for scoping the inventories and for monitoring the local project implementation, and each appointed a liaison officer.

At the end of the project, a compilation of the jointly agreed lessons learned by each party was produced and published in two versions. One version was aimed at self-improvement of the project parties and contained some constructive criticism. As a gesture of fairness, it was issued only to the project parties. The other contained the general lessons of potential value to future projects elsewhere. This paper is based on the latter report.

The background to the project is as follows. The first initiative in Senegal was a well-executed FAO inventory in 1995. FAO then started to seek funding for a disposal project and in 1997 industry committed to provide financial assistance towards the cost of the project. By 1999 no other donors had been secured, but at that time we discovered that the Netherlands Embassy in Dakar was interested in having a public/private partnership three country project, covering not only Senegal but also Cape Verde and Mauritania. This led to the start of the West Africa project.

Four years had elapsed since the time of the inventory and the time delay meant the inventory findings were no longer reliable and so a new inventory became necessary.

The main lessons from this experience are that the finding of funds for such projects can be difficult and time-consuming and a well-planned and coordinated fund-seeking campaign is required in which all key parties participate.

A further 2 years of planning activities, including the appointment of a consultant inventory manager, were required before the project got underway in September 2001. Inventory taking took only 6 months once the project started. After the tender for disposal operations was awarded to SAVA and Tredi, field operations got underway in 2003 and by end 2004 all of the stocks had been shipped to Germany and destroyed.

The following are some of the key lessons learned during the project. They have been distilled from the submissions of the various contributors, where the selection panel considered the submission to be factually correct.

KEY LESSONS

1. An efficient project time and planning tool should be used

These projects are complex undertakings involving multiple and inter-related steps. The discipline of entering the steps, sub-steps and timings into a Gantt chart helps to ensure that activities are not overlooked and that realistic timing is applied. The use of a Gantt chart, with common software used, such as MS Project, also enables all parties to monitor progress and to foresee the consequences of, and to plan for, any deviations that might occur.

2. Who should prepare the inventory?

In this project the undertaking of the inventory was contracted to a hazardous waste company supervised by an Embassy-appointed consultant inventory manager.

The main reasons for doing this were:

- A hazardous waste company has the handling experience and equipment for the moving and categorising of highly contaminated and fragile containers of toxic materials.
- The undertaking of the inventory would give the hazardous waste company the first-hand field knowledge to be able to plan and execute better the implementation of the repacking, cleanup and associated work. This was expected to lead to a better project field plan and lower operational costs.

The arrangement required a linking of contracts because the company that undertook the inventory would also undertake the fieldwork. This arrangement failed when the fieldwork had to be re-tendered after the inventory phase because of an unassociated problem and a new company won the fieldwork. A major part of the benefit was therefore lost.

It was concluded that it is simpler and less expensive to have a single expert consultant undertake the inventory in conjunction with the local counterparts, with the provision that the local counterparts receive pre-work training and are provided with the necessary handling and safety equipment.

3. How to ensure that the country inventory is complete and how to plan for variations?

One of the reasons for having the intimate involvement in a project of the country liaison officer is to ensure the completeness of inventories. During the inventory phase in this project, obsolete stocks beyond government stores were found, held by the sugar industry and a national formulator. At the request of the national government these stocks were included in the project.

Furthermore, even though a careful and seemingly comprehensive inventory had been carried out together with the local counterparts, some other stocks appeared during the implementation phase. Fortunately, a suitable contingency had been built into the project permits at the planning stage and so these variations could be catered for with respect to export/import permissions.

4. Securing stocks after inventory-taking

Some time after undertaking the inventory, some 10 tonnes of stocks in an isolated location disappeared (probably stolen) and were never recovered.

- If during the inventory a potential risk of theft of stocks is identified then steps should be taken to make the stocks more secure. This could include fencing, adding locks to doors, moving to a more secure location or welding closed, with suitable safety precautions, the manlids and valves on external tanks.
- It also re-emphasises the need for a minimum of time between undertaking the inventory and carrying out the fieldwork

5. Data security and back-up

During fieldwork the sub-contractor twice had cameras stolen, together with the contained photo documentation.

Apart from the obvious need for good security for valuable and attractive items such as cameras and laptops, photo records and data MUST be backed-up daily onto not only a local laptop but also onto CD. There MUST also be regular transfer of such data to a central database.

6. Emergency response procedures

After the waste had been shipped to Europe, a solvent odour around some freight containers led to an incident at a European railway station. Police and Fire Brigade took major emergency action, with blockaded public access and evacuation of some people, and the TV and press became involved, until it was confirmed that there was no risk.

The containers contained so-called Big Bags holding contaminated soil. The soil contained small residues of pesticides and solvents. Someone has assumed that the odour was toxic.

The SAVA emergency response procedure was activated by the incident and was able to attend promptly, to provide the necessary information and otherwise to assist, and this resulted in the standing-down of the emergency services. The lesson here is to use only vapour tight shipping containers. The "incident" emphasised the importance of having a good Emergency Response System built into the project.

7. Multi-country approach

The Netherlands Embassy in Dakar had requests for assistance from the three countries, Cape Verde, Senegal and Mauritania and for reasons of efficiency, it decided to include the 3 countries in a single project. This was found to be more economic and efficient than having three separate projects, mainly due to having a common contractor, a single tender, shared mobilisation costs and economy of scale. Furthermore, the quantities of stocks in Cape Verde and would have had to bear unduly heavy associated costs if it had been run separately.

CONCLUSIONS

In conclusion, few previous projects have published a lessons-learned report. The findings of such reports are beneficial to subsequent projects and so there should be an obligation in any project to do conduct and publish a lessons learned exercise. Without this type of review, there will be a reduced potential for capacity building and the opportunity for shared learning. In this project the lessons learned reviews were carried out by the independent project monitor from the Danish consulting firm NIRAS appointed by the Netherlands Embassy and the summary report has been sent to many stakeholders.

ACKNOWLEDGEMENTS

The authors wish to thank Preben Knudsen of NIRAS Consulting Engineers and Planners A/S, Aalborg, Denmark and the Royal Netherlands Embassy, Dakar, Senegal for permission to use materials from the project in the preparation of this paper.

European Crop Protection Association
member of CropLife International

CONTAINER MANAGEMENT ACTIVITIES IN CENTRAL AND EASTERN EUROPE

The European Crop Protection Industry – a Responsible Partner in Agriculture and Society

The European Crop Protection Association (ECPA) represents the crop protection industry in Europe. ECPA is committed to the professional management and stewardship of crop protection products throughout their lifecycle.

The crop protection industry recognises the need to extend best practice to the management of packaging. It does so through numerous industry processes and educational activities designed to minimise risk to people and the environment.

The crop protection industry is committed to initiatives aimed at preventing the accumulation of empty packaging resulting from the use of crop protection products by supporting the establishment of national container management systems.

Industry-run container management schemes are successfully operating in nine European countries, including two in Central and Eastern Europe (Hungary and Poland).

CASE STUDY

COLLECTION SCHEME IN HUNGARY

Hungarian Crop Protection Association (HuCPA)

The Hungarian collection scheme, CSEBER, established in 2003, is a non-profit scheme for the collection of crop protection product packaging.

It is financed by industry on the basis of volume of packaging issued on the market.

Empty, rinsed crop protection product containers are brought by farmers to collection sites. The containers are collected three times a year from 120 collection sites throughout Hungary, and are subsequently transported for incineration and energy recovery. The 2005 target is to collect 1,448 tonnes, which represents 54% of the crop protection product packaging issued on the Hungarian market this year.

CSEBER
csomagolóeszköz begyűjtési rendszer

ECPA CONTAINER MANAGEMENT GUIDELINES

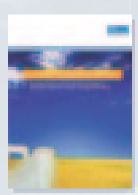
Building effective and integrated strategies for packaging reduction, design, rinsing and recovery

The guidelines provide a comprehensive management approach for the industry's packaging throughout its lifecycle.

The guidelines are intended to help the establishment of effective and integrated container management systems.

The key objective of any container management strategy is to establish a set of practices starting with design and performance criteria for agrochemical packaging and ending with defined routes for recovery of cleaned, empty packaging. The guidelines are based on the following guiding principles:

- Safe packaging
- Safe use
- Packaging mass reduction at source by design
- Safe and sustainable recovery



CASE STUDY

COLLECTION SCHEME IN POLAND

Polish Crop Protection Association (PSOR)

The Polish collection system was initiated in 2004 as a pilot scheme with the aim of collecting 50 tonnes of crop protection product packaging.

The 2005 target is to collect 510 tonnes, which represents 30% of the crop protection packaging foreseen to be issued on the Polish market this year.

The scheme is financed by industry on the basis of packaging issued on the market.

The empty and rinsed packaging is collected every 2-3 months from 1,600 collection sites throughout Poland. The collected packaging is then incinerated with energy recovery.

- Packaging plays a central role in safely delivering crop protection products to the intended targets.
- Recovered packaging is a valuable energy resource that can help reduce the consumption of fossil fuels.
- Energy recovery is a valid strategy for managing used agrochemical packaging.

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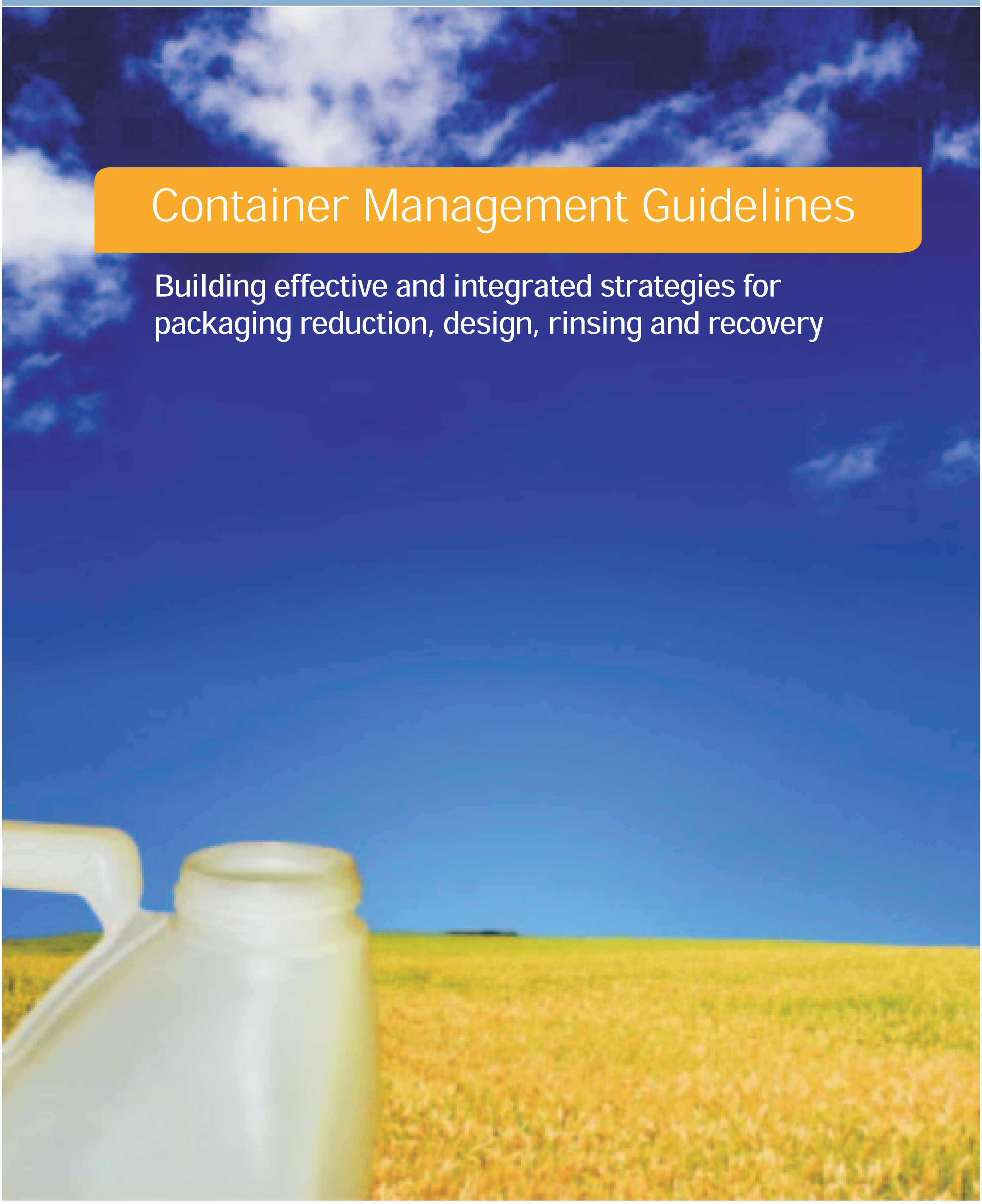


Container Management Guidelines

Building effective and integrated strategies for packaging reduction, design, rinsing and recovery

Contents

1 Introduction: Evolving container management strategies (CMS) in Europe today

Photo courtesy of Pamira

Working together: companies, associations and authorities

This document outlines ECPA's policy on CMS and provides guidelines based on that policy. The guidelines are intended to help national crop protection associations and companies establish their own effective and integrated CMS.

The guidelines are offered on the understanding that where local laws and regulations are already in place, these must take priority. The guidelines can and should, however, be used in dialogue with the relevant authorities to help shape new laws and regulations and revise existing ones.

Two levels of information are provided in the guidelines. The guidelines are provided at a glance in a concise form at the beginning of each section, for those seeking basic information on the rationale behind each container management theme. The guidelines are also provided in depth, for those seeking more detailed and technical information on the themes.

Contributing to environmental sustainability

Crop protection products play a vital role in securing the quantity and quality of the food, feed and fibres required by a growing global population.

Notwithstanding these benefits, the crop protection industry is increasingly expected to provide the scientific research that demonstrates the safety of its products to operators, consumers and particularly the environment.

Packaging plays a central role in safely delivering crop protection products to the intended targets, thereby minimising risk of leakage in the supply chain and exposure to operators.

Packaging also needs to be managed to meet other environmental goals, which have become increasingly important in the context of prevailing societal concerns about environmental sustainability. It follows that the container management strategy presents the industry with an opportunity to show that it strives to be an environmentally responsible partner in agriculture and society.

Consequently, the guidelines are based on the following guiding principles:

- Safe packaging;
- Safe use;
- Waste reduction at source by design;
- Safe and sustainable recovery.

There are many instances where the industry has been highly effective in demonstrating its commitment to Responsible Care by managing its packaging waste in response to escalating public awareness and pending local legislation. However, these schemes have not always resulted in cohesive regional strategies. The purpose of these guidelines is to provide foundations for the development of such strategies.

Legislation on packaging and packaging waste, at both the Member State and European Community (EC Directive 94/62/EC) levels, sets targets for the recovery and recycling of packaging.

The development of comprehensive CMS at the national level by the associations and companies, based on a coherent policy developed at the Brussels level by ECPA, has never been more important than it is today.

Looking to the future

Container management is a dynamic and innovative process. The strategies outlined in this document will address short to mid-term issues relating to the safety of container management. Regular reviews will be necessary to link the present strategies to future technology innovation, which will further enhance the standards of farm chemical operations.

2 ECPA Policy: The fundamentals of a pan-European container management strategy

Preamble

The crop protection industry recognises the need to extend best practice to the management of packaging waste. It does so through various industry processes and educational initiatives designed to minimise risk to people and the environment associated with waste product containers.

Container management strategies (CMS) can only be successful if all stakeholders are fully committed to their development and actively participate in their implementation. The industry therefore strongly encourages co-operation in this field.

ECPA's policy on CMS consists, essentially, of a fundamental series of commitments to action at the Brussels level and recommendations for action at the national level.

These commitments and recommendations are outlined on this page.

Commitments to action at the Brussels level

1. ECPA will maintain both a policy on CMS and guidelines based on that policy.

2. ECPA's Packaging and Transport Expert Group (PTEG) will manage the issues affecting the policy and guidelines, with a view to encouraging a pan-European industry approach that is harmonious, coherent and workable.
Specifically, this will involve:
- Ensuring local country and company requirements are taken into account;
- Annually reviewing performance against objectives.

3. At the national level, ECPA promotes its policy on CMS to the industry and the guidelines provided for the purpose.

4. The ECPA PTEG will work to meet customers' packaging needs and promote the highest priority to operator and environmental safety.

5. ECPA will ensure that national crop protection associations and companies are aware of the need to extend best practice to all packaging activities.
Specifically, this will involve:
- Defining best practice and setting standards for design, registration and use;
- Establishing and maintaining effective communication with country staff involved in packaging so that they can influence European decisions and take local action;
- Publishing clear and concise information via all relevant media;
- Aiming to continuously improve all aspects of the packs the industry offers;
- Developing the practical structure to ensure that the national associations can implement ECPA's policy on container management strategy;
- Participating in packaging committees, teams and conferences to ensure that the industry's views are disseminated;
- Initiate training of staff and customers to ensure that they can safely use and recover or dispose of product packaging.

Recommendations for action at the national level

1. Compliance with the law is paramount. Specifically, for the crop protection industry, this involves:
   - Complying with European directives and local laws on packaging waste and waste disposal;
   - Actively collaborating with regulators to help shape new laws and regulations and revise existing ones.

2. The reduction of packaging is an important starting point. Specifically, for the crop protection industry, this involves:
   - Reducing packaging at source by design, wherever possible;
   - Ensuring that pack weight is consistent with fitness for use, in line with the Essential Requirements. (EC 94/62 Articles 9 and 11 require minimisation of packaging weight and volume consistent with safety, hygiene and environmental considerations).

3. Formulations have an important role to play in container management. For the crop protection industry, this involves providing increasingly innovative formulations that facilitate emptying, rinsing and draining.

4. Designing increasingly innovative packs that facilitate emptying, rinsing and draining is fundamentally important. Specifically, for the crop protection industry, this involves:
   - Ensuring that packaging is designed to be safe to use;
   - Ensuring that packaging and the ultimate disposal of packaging waste are given a high priority during and after product development.

5. Appropriate cleaning of packs at the time of application will be promoted so that packs can be recovered or disposed of safely. This is important and specifically, for the crop protection industry, involves:
   - Advocating the importance of container rinsing as one of the cornerstones of all effective and integrated container management;
   - Actively encouraging farmers to empty, rinse and drain their packs during the application process.

6. Disposal routes that are safe to the operator, the public and the environment need to be encouraged. Specifically, for the crop protection industry, this involves:
   - Seeking agreement from local country regulators that cleaned packaging can be disposed of as non-hazardous waste;
   - Seeking to ensure (based on local country laws and farm practice) safe and closed disposal routes for the industry's packaging waste, including recycling routes, as alternatives to the accepted energy-from-waste option.

Compliance with the law is paramount.

7. Resource conservation goals can be met by respecting a step-wise hierarchy for the management of packaging waste. Specifically, for the crop protection industry, this involves:
   - Respecting a hierarchy of (1) reducing, (2) reusing and (3) recovery and recycling packaging waste;
   - Selecting the best option in the hierarchy on a case-by-case basis, taking into account the technical and economic feasibility of the options in specific circumstances.

8. The key objective of any container management strategy is to establish a set of practices and a defined route for recovery of cleaned, empty packaging waste. Specifically, this set of practices needs to:
   - Be appropriate to specific local circumstances;
   - Evolve in line with improvements in technology, legislation and infrastructure;
   - Be socially, environmentally and economically acceptable.

3 ECPA Guidelines: A strategy-building tool for the European crop protection industry

Getting started

The European crop protection industry is committed to managing its packaging in an environmentally sound way, encouraging resource conservation wherever possible. The guidelines in this document provide a comprehensive management approach for the industry's packaging waste. They include reducing the amount of packaging, developing increasingly intelligent packaging design, and promoting the on-farm rinsing of packaging with a view to ultimate recovery. All of these are essential building blocks of an effective and integrated container management strategy.

3.1 A basic principle: reducing the amount of packaging

A reduction in the amount of packaging placed on the market can be achieved by:

- Product presentation;
- Formulation innovation;
- Reusable packaging.

A reduction in the amount of single-trip packaging requires:

- Optimum pack sizes to meet the farmer's needs better;
- Further advances in pack process technology;
- An optimal choice of materials.

Innovation in new active substances and/or new formulations has already contributed to, and will continue to reduce, the amount of packaging waste.

3.2 Minimising risks: intelligent packaging design

3.2.1 Design at a glance

An integrated approach to packaging design

When designing packaging for crop protection products, it is important to consider the pack, the formulation and application technology as a single entity. The design should ensure that the container/formulation combination can be easily rinsed. The industry has an agreed test method to assess the rinsing characteristics of containers, which facilitates the design of effective container/formulation combinations.

Continuous improvement of packaging design

Most of the currently available pack designs are easy to handle on farms and allow for more complete emptying by avoiding blind corners and other design features that can trap product residues. This should be maintained and further improved by regular company reviews and audits on packaging. In addition to the design features, an appropriate choice of container materials can also help minimise the product residues remaining in the container after rinsing.

For more detailed guidelines on packaging design, see section 3.2.2 (Design in depth).

3.2.2 Design in depth

How to use these guidelines

These guidelines provide standard design criteria for one-trip packs of crop protection products in solid and liquid formulations.

They are intended to help ensure that crop protection products are packed to present a minimum risk to people and the environment. They have been prepared by an ECPA working group of specialists with extensive experience in the field of packaging to help those involved in the various stages of pack procurement (such as design, selection, testing, approval and purchasing).

They will also be of help to national authorities and international organisations.

In these guidelines the word "must" is used to indicate the minimum industry standard acceptable and the word "should" to indicate proven good practice.

These guidelines provide standard design criteria for one-trip packs of crop protection products in solid and liquid formulations.

Basic requirements

- Must comply with all legal requirements where these exist;
- Must comply with transport regulations and pass UN* performance tests where required;
- Must be identified as packaging for crop protection products (for example, by the appropriate labelling);
- Must minimise the possibility of operator contamination in opening, transferring, re-closing and rinsing;
- For a primary pack, or in the case of a combination pack, the packaging system should not exceed 25 kg/20 litres for manual lifting by one person;
- The packaging concept should use a chemical-specific standardised pallet (for example, 1000 x 1200mm, CP1);
- Should drain well and facilitate easy and effective rinsing to maximise product residue removal;
- Opportunities should be taken to develop product packaging that avoids confusion with food or drink packaging;
- Should be capable of passing UN performance tests where these standards are not required by local legislation;
- Should provide appropriate measures to prevent counterfeiting;
- Should offer a simple method of quality control;
- Should facilitate simple and environmentally sound management of packaging waste;
- Consideration should be given to the need for a separate or integral measure facility or graduated scale.

* UN - United Nations Recommendations on the Transport of Dangerous Goods (Model Regulations)

Containers

In general:

- Must be physically adequate to withstand the required filling, transport, storage and use mode;
- Must be product-tight;
- Should have no sharp edges or projections;
- External rims or recesses should not trap product during or after pouring (otherwise ancillary dispensing devices may be needed);
- Should stand up without falling over (in the case of rigid packs);
- The ratio of pack material to product volume should be minimised in line with essential requirements legislation;
- Should be usable for as many different products as possible with standardised and modular formats;
- Empty packaging material should occupy minimum storage space;
- The container should be designed to permit glug-free pouring with minimal dripping or splashing;
- Where a 63mm closure system is used, it should be consistent with agreed ECPA industry standards.

Handles (and/or suitable recesses in the base for large containers):

- Should be provided for rigid packs of more than 5 kg/ litres;
- Should be isolated from the contents (vapour/ liquid phase);
- Should be large enough for a gloved hand;
- Should allow for easy gripping when wet.

Closure:

- Must be leak-proof;
- When intended, re-closure must be safe and liquid-tight;
- Closure must be removable with gloved hands, preferably without tools;
- Should be tamper-evident;
- Must meet the requirements of EC99/45 Article 9 in terms of tightness, compatibility, strength and re-application and resist the normal stresses and strains of handling.

Packaging materials:

- Must be inert to contents;
- Must be an effective barrier against diffusion and migration (water-soluble packs must be packed in waterproof packaging);
- Should be selected with recyclability and/or disposability in mind;
- Should be identified by a coding system;
- Should not be fragile or potentially hazardous.

Labels and printing:

- Material and printing inks must be resistant to the elements, the product and physical damage throughout the storage period;
- Must be firmly attached to the containers;
- Must comply with legal requirements (for example, hazard labelling);
- Should allow adequate space for safety instructions that can be referred to before opening the pack;
- Must survive immersion in sea water where the product category demands it.

3.3 The route to recovery: rinsing on the farm

3.3.1 Rinsing at a glance

Recovery depends on rinsing
Rinsing is a fundamental part of application. Empty chemical containers that have not been properly rinsed and cleaned can pollute the environment and pose a potential threat to public health, animals, and wildlife. Effective on-farm rinsing is therefore an integral building block of all the routes to recovery supported in these guidelines. ECPA is satisfied that properly rinsed containers present no practical hazard within the recovery logistics.

Crop protection associations are therefore advised to actively work towards a non-hazardous waste classification for rinsed containers. This is supported by a number of countries that do classify rinsed containers as non-hazardous waste.

The farm is the best place for rinsing
It is extremely important that the effective rinsing of containers takes place on the farm itself. No matter how an empty container is recovered, it must be properly rinsed. This underpins all subsequent activities. The correct practice for rinsing requires the farmer or spray operator to:

- Rinse the containers immediately after emptying them;
- Add the rinsate to the spray tank.

This allows for effective removal of product residues and, in addition to being good agricultural practice, makes good economic sense by ensuring that users get full value from their purchase.

For more detailed guidelines on rinsing, see section 3.3.2 (Rinsing in depth), below.

3.3.2 Rinsing in depth

How to use these guidelines
These guidelines cover containers for liquid or solid products that are normally diluted with water. All other containers should be disposed of according to the instructions on the product label or through agencies licensed for the purpose.

These guidelines provide three different options for rinsing:

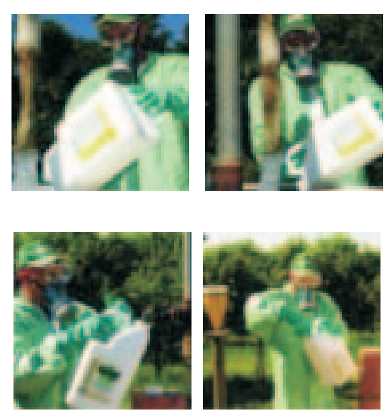
- Triple rinsing;
- Pressure rinsing;
- Integrated rinsing.

Whichever option is selected, responsible rinsing is in the interests of everyone concerned with the handling of crop protection products. Rinsing ensures that excessive product residues are not left in the product containers after use - an essential prerequisite for recovery and for good economic control. Moreover, clean containers minimise the risk of exposure to people, animals, wildlife and the environment.

Triple rinsing
To triple rinse, the operator should allow the contents of the container to drain for an extra 30 seconds when emptying.

Then, 25 to 30 percent of the container's capacity should be filled with clean water. The cap should then be securely re-closed, after which the container should be shaken, rotated, rolled or inverted so that the water reaches all the inside surfaces.

The rinsate should then be drained into the spray tank (the recommended draining time being 30 seconds). This process should be repeated at least twice or until the container is visually clean.

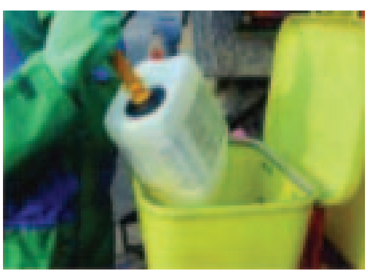


Photographs on this page are courtesy of AdiValor.

Responsible rinsing is in the interests of everyone concerned with the handling of crop protection products.

Pressure rinsing

Pressure rinsing equipment uses water under pressure (typically 3 bar) in the form of a static or rotating spray jet and valve. Some pressure rinsing equipment includes a sharp device that penetrates the container walls for rinsing purposes, thereby offering the additional advantage of preventing the container from being re-used. These devices should be used in accordance with manufacturers' instructions to avoid injury to the operator.



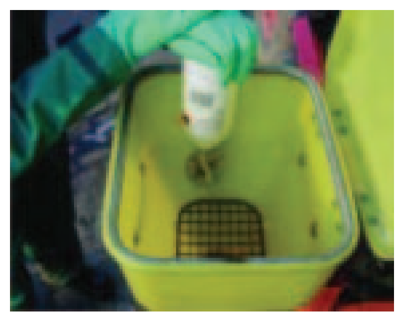
Integrated rinsing

Wherever possible, integrated rinsing equipment should be used. Integrated rinsing is the most efficient method of rinsing containers and provides a high level of operator safety. It is also quicker than both triple rinsing and pressure rinsing.

Integrated rinsing devices rinse by using water under pressure (of typically three to five bar). A static nozzle with a valve is normally built into the induction hopper of the sprayer. The water pressure cleans the container until no residues are visible (typically requiring up to 30 seconds and 15 litres of water). The rinsate is then automatically added to the spray liquid.

Integrated rinsing devices can be built into a closed chemical transfer system and can therefore provide both efficient rinsing and even greater operator safety. This avoids spillage, which may expose the operator to unnecessary risk.

NB: Whatever the selected method of rinsing, the rinsate must always be added to the spray solution. Closures can be rinsed by placing them in the induction hopper. With triple rinsing they are cleaned by the shaking process. In addition, the manufacturer's instructions should be followed when using any rinsing equipment.



Photographs on this page are courtesy of Bayer Crop Scuience.

A comparative assessment of rinsing methods

Advantages

Triple rinsing
- No extra equipment is required
- Can be used in all situations
- No cost

Pressure rinsing
- Residues of less than 0.01%
- Prevents containers from being reused
- Low cost

Integrated rinsing
- Residues of less than 0.01%
- Used for both rigid and flexible packaging
- Simple operation
- With correct use of equipment, negligible risk to the operator
- Rinsate is automatically added to spray mix

Disadvantages

Triple rinsing
- Residues are influenced by operator technique
- Additional operating time is required
- Some risks of endangering the operator
- Is difficult with non-rigid packaging
- The rinsate is not automatically added to the spray mix

Pressure rinsing
- Additional operations required
- Some risks of endangering the operator
- Can only be used with rigid packaging
- The rinsate is not automatically added to the spray mix

Recommendations to industry and associations
- Fill crop protection products into modern packages and continue to standardise on packaging materials that comply with the design criteria in terms of handling, opening, pouring, rinsing and recovery;
- Encourage the spray equipment industry to offer sprayer systems with integrated rinsing devices and to make available a device for retro fitting to older equipment;
- Advise and consult with end users;
- Include rinsing and recovery recommendations on the label;
- Devise promotional programmes to support rinsing initiatives;
- Initiate a certification scheme to identify product pack combinations that are capable of being efficiently rinsed.

3.4 Packaging recovery: considering the options

3.4.1 Recovery at a glance

Focusing on recovery schemes

The crop protection industry strongly supports recovery schemes for packaging waste. They must be feasible in terms of logistics, economics and their environmental impact. Recovery is given prominence in these guidelines because it is a developed option and the communication of best practice in this field is particularly important.

Planning for recovery schemes

Common success criteria

After many years of development, there are several mature and successful container collection and recovery schemes throughout Europe. Experience gained in this field shows us that the most successful schemes share a number of characteristics. Typically, successful recovery schemes feature the following:

- They are economically viable and environmentally safe;
- There is a clearly defined and controlled end-use for the recovered plastic and other packaging materials;
- Containers are rinsed and cleaned before entering the recovery route;
- There is a shared responsibility between all the stakeholders (including the crop protection industry, distributors, retailers, farmers, farmers' unions, custom applicators, local authorities, government environmental agencies and professional waste collection companies);
- There are controlled and supervised collection sites (and waste streams) to avoid dumping of unwanted crop protection product packaging.

Testing the scheme

In order for national crop protection associations to assess the viability of a collection and recovery scheme, the first step is a feasibility study. This will involve both waste management professionals and key stakeholders. If viable, before proceeding to a wider programme, the next step is to organise a limited pilot scheme to test farmer response, container cleanliness, logistics and the costs of recycling and/or energy recovery.

Funding the scheme

Container collection schemes require funding which should reflect the environmental burden. An example is the German PAMIRA scheme, which is based on the amount of packaging each company puts into the market. Costs are borne by all stakeholders involved in the process in ratio to the burden. More information on collection schemes can be obtained from ECPA.

Energy recovery

The preferred approach for final treatment of the packaging waste is energy recovery.

Energy recovery is preferred because:

- It is the best option environmentally, particularly in terms of resource conservation (for plastic and paper-based materials, energy recovery is effectively a form of recycling);
- It assures the highest stewardship, environmental and safety standards (the energy content of the packaging is effectively recycled);
- It is highly versatile across a range of packaging materials;
- It is legally and economically viable, as well as generally available across the EU (entailing only a small development effort).

Material recycling
Material recycling can also be a suitable approach. In Canada, the US and Brazil, for example, specific end-uses have been identified. For this approach, proposed end-uses should receive specific approval by a suitable body of industry experts after an appropriate risk analysis has been completed.

On-farm disposal
Approved recovery schemes are a good approach for managing both empty, rinsed containers and secondary packaging materials. Where suitable schemes are not established, on-farm disposal may be carried out if legally permitted. Extending best practice for on-farm disposal is the most effective way to raise overall standards. On-farm disposal must therefore be carried out according to local regulations and guidance.

Looking at all the options
While the crop protection industry strongly supports recovery schemes, it is recognised that this may not always be the most practical or suitable option. Consequently, there are three waste management options that should be considered (after local assessments of legislation, social and environmental impacts, economics and logistics):

1. Recovery schemes, where they are legal, practicable and economically viable.

2. Inclusion in municipal waste streams, preferably with energy recovery, and provided the necessary safeguards are in place (particular care must be taken to avoid the possibility of crop protection containers being selected for inclusion in unapproved material recycling streams).

3. On-farm disposal, where legally permitted and there is no feasible alternative, observing guidelines for best practice.

All three are sound approaches but need to be carefully implemented. This will require that national crop protection associations collaborate with official bodies to promote best practice and thereby avoid unacceptable practices such as:

- Indefinite accumulation of waste packaging on farms;
- Entry of used packaging material into waste streams lacking the necessary safeguards;
- Non-approved reuse of containers.

The municipal waste stream option does not usually require particular involvement by crop protection associations and companies. These guidelines therefore focus on recovery schemes and on-farm disposal options.

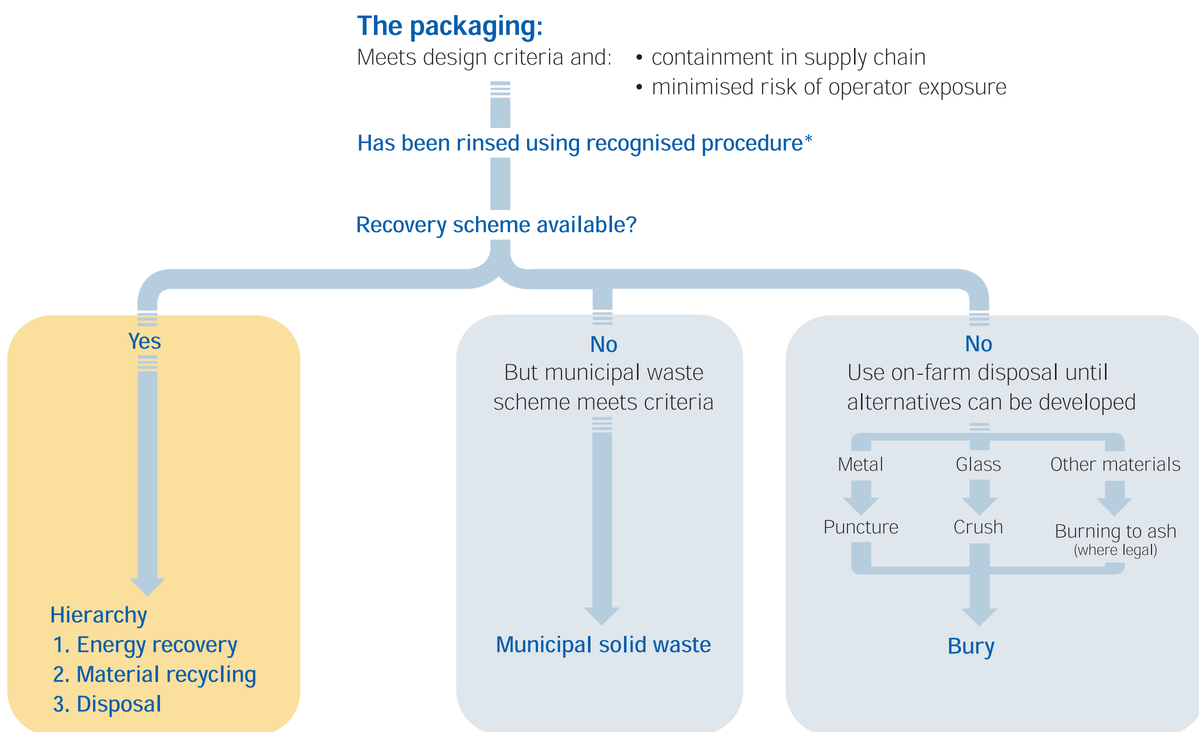
For more detailed guidelines on recovery and other waste management options, see section 3.4.2 (Recovery in depth) and the decision-making flow chart, on next page.

3.4.2 Recovery in depth

Showing the way
Modern society considers waste as a valuable resource that has inherent value as energy. By treatment in a suitable plant, this value can be recovered directly saving consumption of virgin fossil fuels.

The crop protection industry believes that energy recovery is one valid strategy for managing used agrochemical packaging. The industry proposes that, where collection schemes are economically viable and environmentally reasonable (by local assessments of regulatory, social, environmental and economical conditions), energy recovery should be considered the waste management option of choice. Energy recovery from waste effectively means that fossil fuels are exploited not once, but twice. The focus of conservation should be on optimising the use of oil reserves rather than on plastics in isolation.

Decision-making flowchart



This flow-chart is intended to facilitate decision making in the selection of waste management options (for packaging that has satisfied primary design requirements and has been rinsed after use).

* Manual triple rinsing or integrated rinsing preferred.

Energy recovery

The preferred option

In situations where it makes sense to recover empty, rinsed containers of crop protection products, energy recovery is typically the best waste management option. Energy recovery offers all stakeholders in agriculture the most viable solution. It is:

- The environmental option to best utilise resources and minimise pollution;
- Well-regulated and safe;
- Economically viable;
- High-tech but nevertheless available in developing countries.

For resource conservation, the energy-recovery approach is the optimum. As a fuel, the plastic containers that remain when crop protection products have been used are on a par with fossil fuels - and can even replace them in existing facilities with only minor modifications.

For stewardship assurance purposes, energy recovery also affords many benefits. State-of-the-art facilities have to meet very tight regulatory standards and are rigorously monitored.

For versatility, energy recovery stands above all other options. It can incorporate not only plastic containers but all the other materials (such as the outer paper-based packaging and labels). Where energy-recovery options exist, they need only minimal development effort to become operational.

Municipal Solid Waste (MSW)

Municipal Solid Waste (MSW) is necessarily mixed in composition, but within MSW plastics are a particularly rich source of energy - despite the fact they make up a minor proportion of the weight. In the mix, plastics can provide the fuel-power to drive the overall process of energy recovery for MSW.

A rich source of energy, packaging (and particularly plastics) waste can also be used in plants that are already established as generators of heat or electricity. After conversion to a suitable physical form, such as Plastic Derived Fuel (PDF), it can be blended into the process to partially replace virgin fossil fuels. This is called co-combustion. PDF is highly efficient as a substitute fuel (1 kg of PDF replaces at least 1 kg of oil. The energy value (KJ/kg) of plastic being approximately twice that of coal).

Cement kilns

Cement kilns deserve special consideration because:

- Their operating conditions permit waste classified as hazardous to be used as fuel, meaning that very large safety margins exist for rinsed agrochemical packaging;
- They have stringent controls on their emissions, equivalent to those prevailing for toxic waste;
- Energy costs dominate the overall production costs, creating a significant incentive to develop low-cost, alternative fuels (indeed, cement kiln operators often have considerable experience in developing alternative fuels from, for example, car tyres and waste solvent);
- The PDF needs to be in an appropriate physical form;
- Particulates are captured within the process and are built into the final cement product;
- Like agriculture, they are located in rural rather than urban areas;
- They are widely available in both developed and developing countries.

US Environmental Protection Agency (EPA) has looked at the suitability of cement kilns for processing hazardous waste and concluded that replacing coal with solvent-derived fuel "should present no negative effect on the environment or health care in the community, if EPA standards are met". In the US, test burns have been conducted with rinsed agrochemical packaging waste. These confirmed no change from the control emission levels that were within the limits set by federal and local regulations.

The environmental profile of cement kilns is largely positive. One tonne of PDF substitutes more than an equivalent amount of conventional fuels (coal dust, oil or gas). There are no induced additional energy losses in the system - and the energy of plastics can even be used to produce high temperature heat (not only low temperature heat). Moreover, it has been clearly established that combustion of plastics in the high temperature zone does not adversely alter the emissions of the cement kiln.

Cement kilns in practice

After visual control, the rinsed containers are shredded to a preferred particle size of less than 20mm (for relatively flat particles). The location of the shredding facilities is usually based on logistical and cost criteria.

Agrochemical packaging waste is introduced, in shredded form into the main firing (or sinter zone) of the kiln.

Cement kilns produce cement clinker, which involves a final burning step (called sintering) at 1450°C material temperature. Very high flame temperatures of 1800 - 2000°C enable the safe destruction of organic compounds. Traces of residual agrochemicals are efficiently destroyed at very high temperatures and long residence time (at least 5 seconds at a temperature above 1100°C).

Recommended quantities per kiln

- Assumed kiln capacity: 1000 t/d clinker
- Assumed total fuel consumption of kiln: 3.5 - 5 GJ/t clinker
- Recommended fuel substitution rate: 5 - 25% substitution
- Quantity of shredded packaging: 3,8 - 27,8 t/d
- Calorific value recovered: 170 - 1250 GJ/d

NB: The running time of a cement kiln depends on market conditions and the kiln stoppages for maintenance and repairs (usually one month per year). At a running time of 300 d/a, such a 1000 t/d kiln could use about 1100 - 8000 t/a of (agrochemical) packaging. Smaller quantities should be avoided for economic reasons (unless the cement kiln is already equipped with the necessary installation to feed such material into the sinter zone).

To conclude, cement kilns are suitable for the recovery of agrochemical packaging waste because:

- They offer an environmentally acceptable alternative when no dedicated Energy-From-Waste (EFW) facility is available;
- Recovery in cement kilns offers an advantageous recovery value (one-to-one substitution of actually required fuels) - consequently, as a substitution of fossil fuels, it has no adverse effect on carbon dioxide emissions;
- Cement kilns are widely available and the highest demand for cement is in developing countries.

Material recycling

Steel smelting

In the blast furnace method of steel production, hydrocarbons have been used successfully for more than 200 years as reducing agents in the transformation of iron ore into pig iron.

Tests in 1994 concluded that plastics waste can substitute heavy oil. More than 80 per cent of its energy content is used as chemical energy. This method is recognised by the German Environmental Protection Agency as raw materials recycling.

In a comprehensive analytical programme focusing on dioxin and furan contents, no significant increase in waste gas emissions linked to the use of plastics was observed.

The plastics are blown into the blast furnace after shredding the agglomerate to less than 5mm.

Chemical feedstock recovery

It is also possible to convert plastic back into its monomers - the chemical building blocks from which new materials can be made. The process includes effective chemical separation and has an important technical advantage over mechanical recycling in that it can even cope with contaminated or dirty packaging waste where necessary.

However, the technique has relatively high running costs and, because it is highly specialised, requires considerable capital investment. From the technical and economic viewpoints, there are no advantages over energy recovery.

Mechanical recycling

Converting plastics waste into useful new plastic items is generally seen as sensible, where:

- The collected material is clean;
- The collected material does not contain different polymers/laminates;
- There is a market for the product;
- The economics are sound.

The establishment and implementation of container management strategies (CMS) require specific actions at the association and company levels.

3.5 Implementing strategies: a pan-European effort

3.5.1 Crop protection associations

Implementation

The establishment and implementation of container management strategies (CMS) require specific actions at the association and company levels.

Crop protection associations

To begin, associations should:

- Set up a container management task force to establish the strategy and to promote rinsing and recovery campaigns;
- Review the local strategy for agrochemical packaging waste and identifying the local significance (if any) of the pack collection strategy versus the other strategies supported by ECPA.

Then, if significant, associations should set up a task force to:

- Make a broad survey of all possible energy recovery options available within national boundaries, using contacts with the local plastics trade association and official pollution regulators;
- Identify industries with common issues and consider the potential of joint projects.

Associations should also develop a formal project proposal addressing:

- Scope for collaboration with other industries;
- Logistics and economics for the total waste management chain;
- Facilitation of mandatory rinsing prior to recovery;
- Plans for pilot testing;
- Management and funding.

Other key actions at the association level include:

- Auditing current packaging against design criteria (see section 3.2 in these guidelines);
- Discussing campaign principles with authorities to gain their approval and support;
- Gaining specific agreement for a non-hazardous classification;
- Ensuring agrochemical packaging waste is positioned as "valuable PDF" not "problem waste" - ensuring that any discussions on disposal of waste concentrates or active ingredients are kept separate;
- Implementing communications campaigns on rinsing at the farm and dealer levels;
- Defining a communication plan that minimises any unwelcome, negative attention directed at crop protection products;
- Incorporating the recovery of post-consumer packaging waste into education campaigns;
- Conducting surveys to assess attitudes to, and the degree of compliance with, rinsing and recovery scheme requirements;
- Agreeing a budget and funding mechanism;
- Actively networking with other national associations to share information and experience.

Agrochemical companies

Key actions at the company level include:

- Implementing quality container designs;
- Implementing newer technologies that contribute to minimising packaging waste;
- Reducing the amount of packaging placed on the market;
- Promoting best practices for container rinsing and recovery through education programmes, including training of field sales and technical staff;
- Ensuring information on rinsing appears on product labels and instructions for use;
- Preparing to provide appropriate technical information to national associations on rinsing and recovery procedures.

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SUSTAINABLE PERSISTENT ORGANIC POLLUTANTS STOCKPILES MANAGEMENT IN THE REPUBLIC OF MOLDOVA

Valentin Plesca, Andrei Isac, Ion Barbarasa, Larisa Gheorghiev

World Bank/GEF Grant for Preparation of the Sustainable Persistent Organic Pollutants Stockpiles Management Project

ABSTRACT

According to the last studies the most important problem related to POPs pesticides in the Republic of Moldova is that of their intensive application during the previous time and inadequate storage during the last decade, penetrating thus in soils, waters and agricultural products.

There are 780 tones of obsolete and prohibited pesticides with possible content of POPs (DDT, HCB and HCH) out of about 3,000 tones of materials concentrated in more than 340 warehouses. A smaller quantity of heptachlor and polychlorcamphen (toxaphene) has been identified. Other circa 4,000 tones, including 650 tones of DDT and 1,300 tones of HCH are stored in one landfill situated in the south of the country.

Sustainable Persistent Organic Pollutants Stockpiles Management Project financed by the Global Environmental Facility through the World Bank, will complement national ongoing activities in this field, including those on collection and environmentally safe storage of obsolete pesticides in agriculture. The main objective of the project is to prevent the POPs pollution of the environment and to protect human health by the environmentally safe packaging and storage of obsolete pesticides and PCBs; by improving the overall management of POPs; and by creating national capacities for the implementation of the Stockholm Convention requirements, and of those stipulated under other relevant international Conventions and Protocols ratified by Moldova.

It is expected for the project to create strategic partnerships with all stakeholders, including with local public authorities, farmers, other ongoing projects, NGOs, international organizations and potential donors in order to ensure a high level of responsibility at national and local extent in line with objectives as well as to follow up efforts for POPs handling and their step by step reduction.

INTRODUCTION

Mounting evidence of health and environmental damage has focused the attention of the international community on a category of substances referred to as Persistent Organic Pollutants (POPs). Some of these are used as pesticides, while others are industrial chemicals. POPs are also generated unintentionally as byproducts of combustion and industrial processes. POPs possess toxic characteristics which: are persistent, accumulate in the fatty tissues of most living organisms, are prone to long-range transboundary transport, and are likely to cause significant adverse human health or environmental effects near to and distant from their sources.

Due to POPs' persistence and propensity to cross-border movement, countries have sought multinational cooperation to address the challenge. The Stockholm Convention for POPs seeks to eliminate a group of 12 POPs. Under the Convention, which entered into force on May 17, 2004 and was ratified by Moldova on February 19, 2004, parties are required to develop implementation plans to indicate how they will meet their obligations under this Convention. In 2001, Moldova requested from the Global Environment Facility (GEF) financial assistance in fulfilling its Stockholm Convention obligations and received a GEF POPs Enabling Activity (EA) grant. The Moldova National Implementation Plan (NIP) [1] for the Stockholm Convention was one of the main outputs of the project and was approved in October 20, 2004. The NIP identified the POPs chemicals of concern in Moldova as being stockpiles of obsolete pesticides and Polychlorinated Biphenyls (PCBs) contained in electrical equipment, primarily capacitors.

PERSISTENT ORGANIC POLLUTANTS STOCKPILES IN MOLDOVA

POPs Obsolete Pesticides. Moldova has used extremely high amounts of pesticides in the past. Stockpiling of now banned and useless pesticides collectively referred to as "obsolete" pesticides is a significant POPs issue. The stockpiles of POPs obsolete pesticides pose a continuous threat to the environment and public health. In the absence of an obsolete pesticides management strategy, over the years, significant amounts of obsolete pesticides have been stockpiled in warehouses on an ad hoc basis. Often the warehouses are dilapidated; usually the passage of time and exposure has resulted in deterioration of the packaging material. Both increase possibilities for leakage of the toxic materials to the environment – the main pathway for contamination. When obsolete pesticides were placed in storage they were generally indiscriminately mixed with each other in bags and drums. This resulted in a mixture of POPs pesticides with non-POPs pesticides and there is no economically viable way of determining the compositions of all the resultant mixtures in the repackaged plastic and steel drums. Representative sampling analysis indicates that the average amount of POP pesticides out of the total stock of obsolete pesticides is about 20-30%. There are approximately 3,000 tons of obsolete pesticides stored in warehouses in Moldova. Studies have shown conclusively that these materials have contaminated the sites and surrounding soils and nearby surface waters. Other circa 4000 tones, including 650 tones of DDT and 1,300 tones of HCH are stored in one landfill situated in the south of the country.

In November 2003, the Ministry of Defence (MOD) and the State Department of Emergency Situations (SDES) initiated the repackaging and transportation of the obsolete pesticide stocks from some 344 warehouses scattered across the country, to 37 centralized district storage facilities, one in each of the administrative districts. These warehouses were selected based on a number of criteria to ensure safety and security. The warehouses were each examined during the Environmental Assessment of the project to evaluate their integrity. While this system of centralizing the storage is an improvement it is not a long-term solution. Centralizing the materials allows for improved security and monitoring and will facilitate ultimate disposal. The repackaging, transport and storage activity has been, and will continue to be until completion, co-financed by NATO. All of the obsolete pesticides will be relocated to the 37 warehouses.

PCBs and PCB-containing electrical equipment. Moldova has an unusually high amount of PCBs requiring disposal because in former Soviet Union times it was the energy hub transmitting electricity to Bulgaria. Most of the PCBs in Moldova are concentrated in electrical power installations where the dielectric oils in capacitors and transformers contain PCBs. Most of this equipment is out of use but still in place. The main pathways of environmental pollution are PCB containing oil spills and leaks from electrical equipment no longer in use. The capacitors at power installations are situated outdoors and PCBs leak from corroded capacitors to the soil below the capacitor batteries. Twenty thousand PCB-containing capacitors, now unused and referred to as “discarded,” are located in 20 electrical substations throughout the country but most (12,000) are at the Vulcanesti Power station where there are also two dumps with approximately 2,000 broken capacitors. The total PCB content in oils within the 20000 capacitors (excluding the pits at Vulcanesti) is estimated at 380 tons while the total weight of the capacitors is approximately 1,060 tons. Since PCBs are mobile in the soil the contamination can spread. The PCB-containing capacitors in the electrical substations are in a condition where leakages, due to corrosion, are occurring and leakages are expected to increase in the coming years. Analysis has determined very high levels of PCB contamination at the capacitor sites primarily at Vulcanesti where the 10,000 m^2 of soil underneath this assemblage, to a depth of 60 cm, has been found to be contaminated with PCBs.

An inventory of capacitors held by users of electricity has not been undertaken as yet, but based on expert judgments the total PCB-content of those capacitors is roughly estimated at approximately 20-50 tons. A detailed inventory of PCBs in transformers, switches and other electrical equipment has not been finalized but according to a preliminary inventory about 30,000 tons of dielectric oils are used in electrical power installations.

REGULATORY AND INSTITUTIONAL CAPACITIES

From a regulatory and institutional perspective Moldova does not have any specific requirements for the management and control of POPs, but to a certain extent some of the requirements of the Stockholm Convention are covered in a general sense under existing legislation and institutional arrangements. The Ministry of Ecology and Natural Resources (MENR) is the central national environmental authority which has been designated the Stockholm Convention competent authority and as such is responsible for coordinating the POPs related activities of the following government bodies involved in chemicals management issues: Ministry of Health, Ministry of Agriculture and Food Industry, Ministry of Industry, Ministry of Energy, Ministry of Economy, Ministry of Internal Affairs, Ministry of Defence, Department of Customs, Department of Standardization and Metrology, and the Department for Emergency Situations. Local authorities have responsibilities for environmental protection and management in the limits of their territory. A National Coordinating Committee (NCC) for implementation of the Stockholm Convention, with MENR, as the lead agency, has been established to provide overall guidance and coordination for POPs NIP development.

The MENR is responsible for developing the NIP and for compliance and enforcement of national legal requirements and international obligations related to management of toxic and hazardous products and substances. Capacity for enforcement of provisions of the Articles covered under the Convention is currently non existent in Moldova. The NIP has identified the need for a gap analysis of existing legislative requirements for POPs to bring them in line with that of the Convention and comparable to those in EU countries for POPs and other toxic chemicals and wastes.

INTERNATIONAL SUPPORT OF POPs ACTIVITIES

The efforts of Moldova in implementing the provisions of the Stockholm Convention and the results of the POPs Enabling Activity Project have motivated the GEF to finance the next grant for preparation of Sustainable Persistent Organic Pollutants Stockpiles Management Project, which will complement national ongoing activities in this field, including those on collection and environmentally safe storage of obsolete pesticides in agriculture.

The GEF Implementing Agency of the project is the World Bank. The Bank has been very active in supporting Moldova in improving its environmental management capabilities and in incorporating environmental and social concerns into its sector operations. The proposed project is consistent with the Bank’s Environment Strategy and 2005 Country Assistance Strategy (CAS) for Moldova. The key pillars of the strategy are improving people’s quality of life, quality of economic growth, and quality of regional and global commons. The Bank’s technical knowledge on POPs management and its experience in the design and implementation of GEF investment projects give it a comparative advantage among the GEF Implementing Agencies in providing this assistance.

PROJECT OBJECTIVES AND BENEFITS

The project will contribute to both national and global objectives. On the national level, it will support implementation of the country’s *Economic Growth and Poverty Reduction Strategy Paper*, which has several references to POPs, and its action plan proposes interventions in the area of obsolete pesticides and PCBs, along with the recognition of the need to strengthen institutional capacity in this area. The implementation of proposed activities would provide many *local benefits* by reducing the impact of POPs on public health and environment. The project would address land degradation by preventing further soil pollution by various POPs.

The project will serve as a triggering mechanism for modernization of the current national chemicals management system steering it towards environmentally sound management of toxic, persistent, harmful and bio-accumulative substances in all spheres of human society. Minimization and final elimination of POPs related pressures and impacts to the natural and human environment is an integral part of national environmental policy. It is considered that environmentally sound management of chemicals, if being adequately set up and functioning, is an important element which contributes to a well-being of the country, society sustainable development and poverty alleviation. Resolution of POPs pesticides problems, as well as sound management of other prohibited and unused agricultural chemicals, is considered to be helpful for promotion of Moldovan ecologically clean agricultural products world wide.

The project will also provide the following global benefits: reduced threats on biological diversity – the elimination of POPs stockpiles and their sound management would decrease both the global pollutant burden and possible impacts on wildlife, domestic animals and humans; and improved transboundary water quality – by ensuring sustainable POPs management, the project will contribute to the prevention of future contamination and threats to the quality of the global hydrological regime. It will also contribute to the objectives of two other international environmental agreements – the Basel Convention on the Control of Trans-boundary Movements of Hazardous Wastes and Their Disposal and the Rotterdam Convention on the Prior Informed Consent Procedures for Certain Hazardous Chemicals.

The *main development objective* of the project would be to protect the environment and human health by safely managing and disposing of stockpiles of POPs contaminated pesticides and PCBs.

The *global project objective* of the project is sustainable POPs stockpiles management and strengthening of the regulatory and intuitional arrangements for long term control of POPs and other toxic substances in line with the requirements of the Stockholm Convention and other related conventions and protocols ratified by Moldova. To track the progress toward achieving this development objective, the project will use four key results indicators as summarized below:

- reduced risks of POPs environmental pollution to human health by safely storing and disposing of stockpiles of POPs contaminated pesticides and PCBs;
- destruction of 2,210 tons of PCBs and POPs containing and contaminated obsolete pesticides;
- modern regulatory system established within Moldova for the management and control of POPs and other toxic and harmful chemicals and wastes;
- institutional and human capacities for enforcement of the POPs regulatory framework and for sustainable POPs stockpiles management strengthened.

PROJECT COMPONENTS

The project consists of three components: Management and Destruction of POPs; Development of a Regulatory Framework for PCB Management and Control; and Institution Strengthening and Project Management.

Management and Destruction of POPs 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) and management of PCBs and destruction of obsolete capacitor stockpiles (19,300 capacitors – approximately 1,060 tons) by incineration.

Strengthening the Regulatory Framework and Capacity Building for POPs Management includes actions for modernization of current legislation specifically related to the Stockholm Convention and incorporation of provisions for establishing a broader chemical safety approach in the country based on EU directives. Full transposition of all relevant EU legal acts shall be achieved.

Institutional Strengthening and Project Management Support foresees strengthening of the MENR's capacity for POPs management and includes developing of the Information Management and Reporting System for POPs; POPs Monitoring Network; Identification of POPs residuals and Mapping of Polluted Areas; and POPs Awareness and Educational Activities.

SUSTAINABILITY AND REPLICABILITY

As a Party to the Stockholm Convention, Moldova is obligated to identify, manage, and dispose of POPs in an environmentally sound manner. With the destruction of about 30% of the stocks of POPs contaminated obsolete and banned pesticides and approximately 80% destruction of the PCB's in the country, Moldova will have taken a large step in meeting its POPs convention commitments. Financing for the destruction of the remainder of the obsolete pesticides is being determined. For the remaining 20% of the PCBs in electrical equipment which is scattered through out the country the project will support the introduction of a comprehensive legal and institutional framework for POPs and dangerous substances consistent with the EU Directives for these substances. This will lead to the establishment of a national inventory of holders of PCB containing and contaminated equipment and a management plan for the ultimate disposal of this stock of PCB's according to the program set out in the Convention.

The sustainable management of this residual stock of PCB's will be assured with the support of the capacity building activities of the project, which will provide training of inspectors in all aspects of PCB enforcement, management and control and in establishing inspector networks across the country along the lines of the EU's IMPEL-TFS. In addition the strengthening of the analytical capabilities of key laboratories in PCB and POPs measurements will allow inspectors and other regulators to track POPs in equipment, in process, in emissions and in the environment. A comprehensive system of POPs regulation, testing, enforcement, management, data storage and information exchange will be put in place to assure the Convention Parties of Moldova's commitment to the complete elimination of POPs in the country and the protection of its people and the environment.

This project will build upon other related and ongoing POPs projects. These include: development of a National Implementation Plan for the Stockholm Convention, which has been completed with GEF funding; the ongoing NATO projects to set up a dedicated laboratory for POPs analysis and repackage, transport and destroy obsolete pesticides; and repackaging of obsolete pesticides under the direction of MAFI. These activities have already provided useful information which has been used in the development of this project.

This project does not seek to introduce a new approach to POPs management and control, but uses well established models from the experience of other countries. Since the project targets the whole country, internal replicability does not apply as it would in a much larger country where one province or state was initially targeted for POPs phase out. However, as a country model the approach adopted would be replicable in other relatively countries with strong central government systems.

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CONTROL SYSTEM IN THE FIELD OF PROCEEDING WITH PESTICIDES IN POLAND

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ABSTRACT

There are three fields in which pesticide handling can be controlled in Poland:

1. Usage of pesticide
2. Dealing with pesticides' packaging and packaging waste
3. Storage and disposal of obsolete pesticides

Based on the Act of December 18, 2003 on plants protection, the supervision of the use of pesticides is the task of State Inspection for Seed and Plants Health.

According to the Act of May 11, 2001 on packaging and packaging waste, a producer, importer or the person placing on the market very toxic and toxic pesticides is requested to collect a deposit in the order of 10 and 30 % of the value of the goods in the packaging. The Trade Inspection supervises this activity. Proceeding with such kind of waste is restricted and depends on the sort of pesticide residue.

The general supervision of the proceeding with the packaging from pesticides is held by Inspection for Environmental Protection, based on the Act of July 20, 1991 on the Inspection for Environmental Protection.

The used-up pesticides are stored in special underground pesticide tombs called "mogilniki". These places pose a hazard, which can lead to serious emergency events and this is the reason for the Inspection for Environmental Protection to maintain a special supervision of them. Generally, the Inspection for Environmental Protection performs the supervision of pesticide storage, waste and packaging, not of the use of pesticides.

There is an initiative currently under discussion in Poland in order to find the simplest way of dealing with pesticides packaging – to create one organisation for all pesticide suppliers and to establish a system of collecting the packaging without deposits. The Minister of Environmental Protection will decide whether to agree on this or not.

Keywords: pesticides, plant protection products (PPP), inspection, control, packaging, waste

INTRODUCTION

To check whether entities obey legal requirements in the scope of pesticides usage, dealing with pesticide packaging and packaging waste and storage and disposal of obsolete pesticides, the Inspection for Seed and Plants Health, the Inspection for Environmental Protection and the Trade Inspection have performed controls of soil, plant and PPP samples as well as documentation investigations. The results of "the physical" controls have turned up better than the documentation results.

There are three fields of controlling the proceeding with pesticides in Poland: 1) usage of pesticides, 2) dealing with pesticides packaging and packaging waste and 3) storage and disposal of obsolete pesticides.

1. Usage of pesticides

Based on the Act from December 18, 2003 on plants protection, the supervision of the use of pesticides is the task of the State Inspection for Seed and Plants Health.

The supervision covers:

1. issuing of permissions and control of entity dealing with re-packing and marketing of plant protection products (PPP),
2. quality control of PPP allowed for marketing purposes,
3. control with proper usage of PPP,
4. authorization of organizational units for checking sprayers used for PPP application as well as supervision of conducting those checks and on technical state of the equipment used for those checks,
5. authorization of organizational units for conducting of training as well as supervision of this training,

6. control of organizational units authorized for conducting PPP efficiency testing,

7. monitoring of PPP usage.

The supervision of fulfilling the Inspection duties mentioned above is performed by the Minister of Agriculture and Rural Development.

Duties of the Inspection are performed by:

1) Chief Inspector

2) Voivode with the assistance of Voivode Inspector as the head of Voivode Inspection for Seed and Plants Health, which forms part of the joint governmental administration.

The Chief Inspector cooperates with and represents the Inspection before the European Union (EU) authorities or other countries or international organizations (of which Poland is a member), dealing with the Health issues.

The Chief Inspector provides any information demanded by the European Commission (EC) in the field of plants protection and seed.

The Chief Inspector can appeal to the EC to obtain the financial support for the phytosanitary purposes and he is responsible for spending this money in accordance with the rules.

The activity of the Inspection in the most restrictive scope presents Figure 1. As it is shown, the amount of withdrawn PPP has decreased over the last years.

The data from 1997-2002 analysis revealed that the PPP decrease in 1997-1999 was first of all caused by a decline in withdrawn PPP due to lack of permits or being out-of-date. 95% of the out-of-date PPP was placed back on the market after new tests and obtaining of re-permits. The reasons for PPP withdrawal from the market and usage are shown in Figure 2.

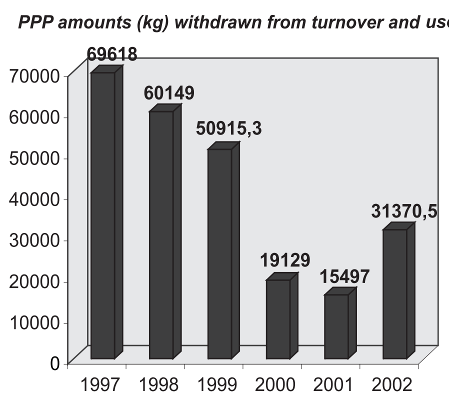

Figure 1: Changes of PPP withdrawal during years 1997-2002 (after Zych, 2002)

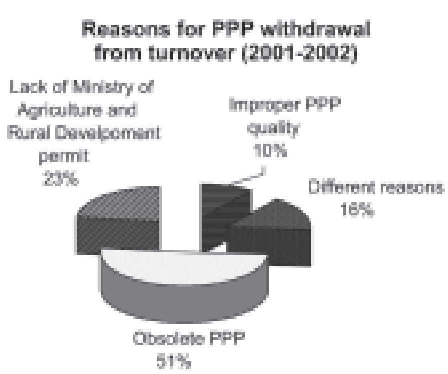

Figure 2: Reasons for PPP withdrawal from the market (2001-2002) (after Zych, 2002)

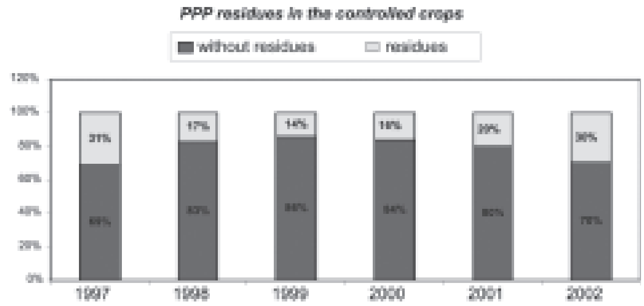

Figure 3: Changes of PPP residues in years 1997-2002 (after Zych, 2002)

As far as PPP usage control is concerned on behalf of the Inspection it is worthwhile to emphasize that in the last few years the PPP residues were stated in samples of controlled plants, though at very low level (0,1-0,4%) – see Figure 3.

2. Pesticides packaging and packaging waste

There are three types of pesticides packaging: single units, collective and those for shipping purposes. Direct packaging having contained pesticides, containing the residues of hazardous substances or polluted by them is classified as hazardous waste. Managing such kind of waste is restricted and depends on the type of residue. Non-direct packaging should be treated like any other packaging waste. Details in regulations of pesticides-packaging waste are described in the Act from April 27, 2001 on waste.

The general supervision of proceeding with pesticides packaging is held by the Inspection for Environmental Protection based on the Act from July 20, 1991 on the Inspection for Environmental Protection.

Inspection duties are performed by the following authorities:

1) Chief Inspector for Environmental Protection

2) Voivode with assistance of the Voivode Inspector as the head of Voivode Inspection for Environmental Protection (forms part of the joint governmental administration)

The Inspection verifies the fulfilment of the following duties:

- disposal of the packaging after very toxic and toxic pesticides listed in the Act from July 12, 1995 on the arable plants protection (cannot be recycled, have to be neutralised only in the precisely described processes)
- other packaging waste recycling
- use of packaging according to legal requirements
- packaging labelling
- reporting to proper authorities

The three ways of fulfilling the duty for proper recycling are shown in Figure 1.

However, not even packaging for substances not classified as very toxic or toxic are meant for recycling.

Entrepreneurs are required to reduce both the amount and negative impact on the environment of the substances used in packaging production. It covers:

- reducing the volume of packaging to the minimum required for its function
- maximum sum of some heavy metals (Pb, Cd, Hg, Cr) / lead, cadmium, mercury and chromium cannot exceed 100 mg/kg [100 ppm]
- other substances hazardous to human health or environment should possibly be reduced

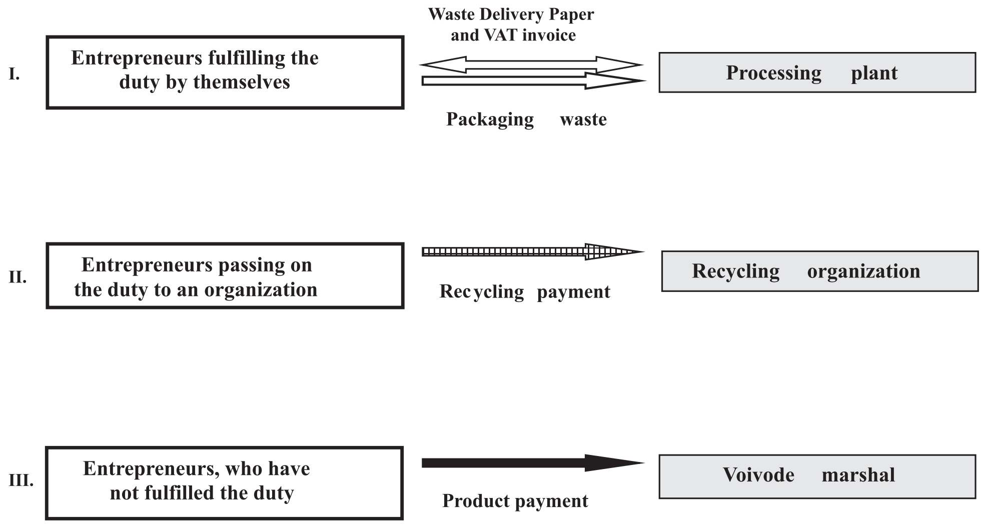

Figure 4: Ways for fulfilment of the achievement of proper recycling level duty (after Zakowska, 2003)

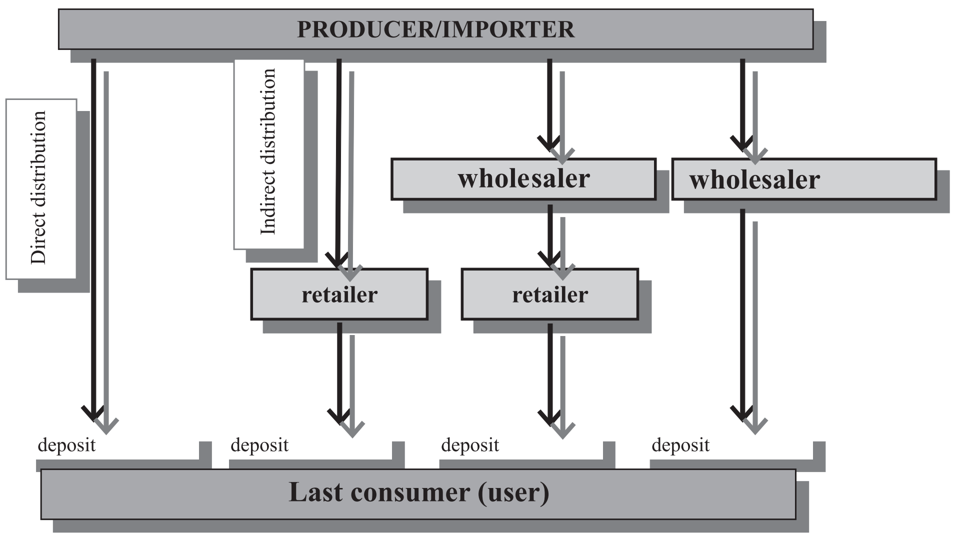

Figure 5: Deposit collecting stage depending on distribution channel (after Zakowska, 2003)

• packaging should be easy to recycle or to use again.

These requirements should be put into practice according to Directive 94/62/EC and the Polish regulations.

The way of labelling is described in the Minister of Environment's Regulation dated April 23, 2004 on the patterns for packaging labelling.

According to the Act from May 11, 2001 on packaging and packaging waste, a producer, importer or the person placing on the market very toxic and toxic pesticides has to establish the deposit in amount of 10-30% of the value of the goods in the packaging (Figure 5). The supervision of fulfilling this requirement is carried out by the Trade Inspection.

Producer, importer or the person placing hazardous substances on the market is required to collect the packaging proper for multiple use as well as packaging waste from a final seller and give him back the deposit.

If the return of deposit to the user by the final seller is impossible due to a break or termination of his business, then producer, importer or the person placing hazardous substances on the market is required to collect the packaging proper for multiple use as well as packaging waste from the user and give him back the money.

Minister of Health in cooperation with Minister of Environment is authorized to issue a regulation with a list of hazardous substances packaging for which deposits could be in different amount than mentioned above due to their specific qualities.

Voivode Inspectorates for Environmental Protection have recently performed a set of 66 controls of units dealing with PPP and fertilizers turnover and 29 controls of farms. The irregularities have been stated in 61 controlled entities (64%). The irregularities concerned:

• legal aspects of dealing with packaging (26 units)

• lack of waste register (26 units)

• lack of combined information for authorities on waste production and management (32 units)

• lack of permits for collecting and shipment of packaging waste after chemicals (4 units)

• delivery of packaging waste after plant protection products to the unauthorised units (3 units)

• delivery of packaging after chemicals without a proper selection to municipal landfills (3 units)

• burning packaging waste after chemicals on the entity's square and in a stove (1 unit).

	Voivodeship	*Mogilniki* – number and sort 31.12.2003		*Mogilniki* – number and sort 31.12.2004		*Mogilniki* liquidation 2004	Controls number 2004	Post-control recommendations number 2004
		Pits	Concrete constructi ons	Pits	Concrete constructi ons			
1	2	3	4	5	6	7	8	9
1	dolnośląskie	0	8	0	7	1	1	0
2	kujawsko-pomorskie	0	17		17	0	5	1
3	lubelskie	0	0	0	0	0	0	0
4	lubuskie	0	0	0	0	0	0	0
5	łódzkie	5	18	5	17	1	4	2
6	małopolskie	20	2	20	1	1	0	0
7	mazowieckie	2	10	2	10	0	8	6
8	opolskie	0	2	0	2	0	2	2
9	podlaskie	0	1	0	1	0	2	0
10	podkarpackie	0	1	0	1	0	0	0
11	pomorskie	0	5	0	3	2	2	0
12	śląskie	1	6	1	5	1	1	1
13	świętokrzyskie	5	1	0	0	6	6	0
14	warmińsko-mazurskie	0	17	0	17	0	0	0
15	wielkopolskie	3	15	2	15	1	1	0
16	zachodniopo-morskie	0	27	0	27	0	0	0
	Total	**36**	**130**	**30**	**123**	**13**	**32**	**12**

Figure 6: Liquidation of mogilniki in each of the voivode in year 2004 (after: Voivode Inspectorates for Environmental Protection)

3. Obsolete pesticides storage and damage

The obsolete pesticides are stored in special underground pesticide tombs called mogilniki. These places pose a hazard, which can lead to serious emergency events and therefore the Inspection for Environmental Protection maintains the special supervision of them.

In 2002, 55 mogilniki controls were conducted. The data on inspection results in 2003-2004 is presented in the table with mogilniki.

As for December 31, 2004, there were 153 mogilniki in total in Poland.

During the inspections, the following assessments were made:

- protection and the notice-board state
- need for underground water and soil sample analysis for pesticide contents
- technical condition
- supervision over liquidated mogilniki.

Generally, the Inspection for Environmental Protection does not perform supervision of pesticide use but only of their storage, packaging and waste.

There is yet another area of IEP pesticides proceeding control – the supervision of transboundary movement of pesticides waste. In 2003, Chief Inspection for Environmental Protection issued only 3 permits for pesticide export to Belgium and Germany. The total amount of exported pesticides was 7000 tons. The Inspectorate however has not received any feedback if the exporters had benefited from the permits.

Pesticides covered by the Stockholm Convention have been produced between 1949 and 1978. Currently these pesticides are not produced in Poland.

There is an initiative, which the Polish Association for Plant Protection is currently discussing in order to settle the simplest way of dealing with pesticides packaging – to found a common organisation of all pesticides suppliers and to establish a system of packaging collecting without deposits. The project assumes that there will be established one company collecting packaging from final sellers without agency of producers, importers or wholesalers. Producers, importers and wholesalers would pay to the company according to an agreement. Retailers would not have to pay to them and collect the money from users. It would simplify the tax policy in the area. The Minister of Environmental Protection will decide whether to agree on this or not.

DEVELOPMENT OF PILOT PROJECT “MANAGEMENT AND DESTRUCTION OF OBSOLETE PESTICIDES IN PILOT OBLASTS IN UKRAINE (CHERKASSY AND L’VIV OBLAST”)

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The proper disposal of toxic substances and persistent organic pollutants in particular, is a vital question all over the world. There are about 500,000 tons of obsolete pesticides accumulated in the world today, and about 20,000 of them are in Ukraine. Ukraine is taking active part in forming a translational environmental safety policy and implementing the principles of sustainable growth, which require a well-balanced ecological aid approach to a proper use of natural resources.

The importance and gravity of this problem is determined by a huge amount of accumulated pesticides, their location on the territory of Ukraine, absence of any control of the access to obsolete pesticides and risk of using banned pesticides, non- proper conditions of their storage and packing, etc. The problem of obsolete pesticide destructions is complicated by the absence of a proper obsolete pesticide management and destruction model, by lack of trained staff and analytical works, part of which is very complicated and expensive, and by lack of coordination within many of the governmental departments.

The American EPA and three Ukrainian Institutes decided in the autumn 2005 that they would implement a pilot project: “Management and Destruction of Obsolete Pesticides in Pilot Oblasts in Ukraine (Cherkassy and L’viv Oblast” . The aim of this project was to assess the level of risks of such stocks to the environment, and to elaborate a typical model for obsolete pesticide management and destruction. In addition, during project implementation some local specialists are trained in managing pesticides stocks, and the cost of the aforesaid works will be defined. The project also foresees a close cooperation with appropriate local authorities with the purpose of informing the population of environmental protection issues, and increasing their awareness of ecological behaviour.

A distinctive feature of the project is a thorough scientific analysis of each stage of the project, as all works will be carried out with the use of dangerous substances that are toxic to humans and the environment. Project implementation includes the following stages:

– elaboration of thorough plan of operation

– identification and inventory of obsolete pesticides at six stocks

– cleaning up the stocks (by re-packing, rendering harmless, and in some cases by using pesticides under control or by destroying it)

– remediation of the soil near stock

– making analysis of the results and developing a typical model of obsolete pesticides stock management.

The project had the following distinctions:

– As object we chose small and medium obsolete pesticide warehouses. Principal objective: to develop maximum clear recommendations on sorting for owners of small warehouses, and estimate the entire work chain – from entering to the complete sorting;

– Search for technologies and ways of the safest and financially most feasible disposal of obsolete pesticides;

– To push research on soil remediation, and to develop technologies adapted to certain territories;

– Development of proposals on prevention of obsolete pesticide accumulation and improvement of post-registration stewardship of pesticides.

Since the beginning of project implementation, we have carried out substance identification from selected stocks, in total more than 300 analyses. As for analyses of plants growing near the stockpiles, they show that the highest level of chlororganic pesticides (DDT group, DDD and DDE) is observed in Settaria. We have been continuing our analytical study for residues of pesticides in plants and soils. We have carried out repacking of obsolete pesticides on three selected stocks in L’viv oblast, followed by transportation and destruction. We also started a study on pesticide destruction using microbes and testing some plant species for our future phyto-remediation study.

We hope that step by step we will clean up obsolete pesticides stocks and the affected land.

Photo 1: Obsolete Pesticides stock in L’viv region before clean-up

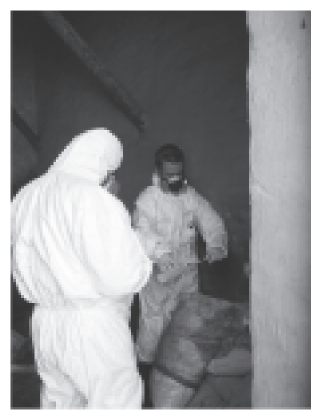

Photo2: Showing sampling works in stores

Photo 3: OP stock in L’viv region after clean-up. Last bags in the corner before loading and shipping for disposal

PESTICIDES (UNUSED, OLD AND PROHIBITED) – CONDITION, STORAGE AND METHODS FOR DESTRUCTION

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The problem with pesticides has arisen immediately since 1969 when Bulgaria signed Agreement for prohibition of the manufacture, trade and use of the pesticides which are the subject of this forum. Since then, up to 1989 measures for destruction or realization in other countries (where these products had not been prohibited) had not been undertaken.

It is known that risk for population and environment does not ensue only from the fact that pesticides included in the food chain could seriously harm the human body. Improper destruction could lead to even more damages than irregular use. During the process of destruction dioxins and other toxic substances could be emitted which are more dangerous for humans and environment. Since 1989, the problem has occurred after the liquidation of ex-agricultural and industrial complexes and leaving large amounts of pesticides with toxicity commensurable to chemical warfare agents without control.

The conclusion for these processes is to suspend aimless funding for repair and repackaging of pesticides and to ensure durable and safe storage. Such activities were applied in Knezha, Popovo and other towns.

The problem with unused pesticides was neglected (consciously or unconsciously) in the Law for restitution of agricultural lands which reflected negatively on the whole spectrum of problems engendering:

– Non-ownership of storehouses;

– Stealing of pesticides and none regulated sale;

– Destroying of storehouses and spillage of pesticides in environment;

– Burying of pesticides and endangering of water horizons for drinking water and rivers;

– Use of prohibited pesticides ensuing from lack of efficient control.

Last but not least we should mark the negative understanding of the problem from the Ministry of Agriculture and Forests (National Service for Pesticides in the past). Opportunities for destruction of pesticides were investigated then proper storage followed by destruction. This led to precondition for a period of 5-6 years delay of activities. The idea for the construction of a Bulgarian prototype for the destruction of pesticides was a complete fiasco. Persons in charge for ordering and realization of the project were not acquainted with the aims and result of the issue. With the help and cooperation of the Ministry of Labor and Social Policy, the Ministry of Environment and Water, the Ministry of Health and the State Agency for Civil Protection the introduction for exploitation of the installation with a doubtful quality and a lack of control for emissions was denied. No allowance was given to start with equipment with absence of warranty for control of processes and of assessment of the effects to the environment.

Meanwhile some extremely unserious installations for possible destruction of pesticides, offered by incorrect firms providing improper information to the competent authorities, were denied. The reason for the outcast was inefficiency and imperfect technical decisions. However, a long time had to pas to reach the idea first to use safe storage of pesticides and then to look for opportunities for destruction.

The idea for storage in BB-cubes is a rational solution on this stage due to the following reasons:

1. Safety of the method guaranteed.
2. Conditions for continued and safe conservation.
3. No need of additional expenses for storage after sealing in BB-cubes.
4. Absence of toxic emissions in the environment.
5. Stability of BB-cubes against external effects and subversive activities.

It should be marked that the majority of the prohibited unused and old pesticides are mixed and available chemical methods for destruction could not be applied. The question about storage of old liquid pesticides is problematic, because in case repackaging could not be implemented they could seriously pollute storage and neighboring areas.

The possibility for storage of pesticides in storehouses built 30-40 years ago is limited. It is not advisable and financially profitable to restore buildings which could not be secured and to become object of crime. There are dozens of cases known of stolen and spilled pesticides in such storehouses.

In the process of research a serious problem has arisen. The question deals about the efforts of the interdepartmental council for old pesticides which were not applied effectively by the authorities on county and municipal level.

The exact reason is that the interdepartmental council in some cases covers the expenses for restoration of storehouses as well as funds the repackaging. Consequently the restored stock has become an appetizing property which the mayor or other owners sell. The conditions in the contract that the new owner should store the pesticides for 3 years could hardly be protected. The owner usually lays down the terms to receive additional rent or to throw out the pesticides. In all such cases the owner usually does not have an individual license to work with pesticides.

In the past 5 years a large scale research was carried out for the sustainable organic pollutants in the country. The results of the research, as well as the conclusion of the experts were definitely negative. Despite the measures undertaken and adopted amendments in legislation, a number of problems still remain to be solved. It is time for development of a total concept and policy to solve the problems. The Ministry of Environment and Water has a position concerning the problems encountered and the construction of installation for destruction of pesticides which will solve all the questions.

Three principles should be followed:

– Conditions for long lasting and safe storage;

– Guaranteed methods for destruction (obligatory in incinerators);

– Control of the emissions in environment with attention to dioxins.

This should not exclude search for other methods taking in consideration the above listed principles.

Utilization of stored pesticides in BB-cubes and others in storehouses will meet serous problems. Most of the pesticides (excluding liquid products) are mixed with additives and the active substances vary from 10 to 15 percent. Exactly these additives are a serious obstacle for destruction of these products in incinerators because in many cases these are silicates or other mineral compounds which could melt, glaze and block the incinerator. This could lead to implementation of preliminary separation of active substance from inert additive and consequent destruction. Thus the cost of the processing will increase. In addition for mixed products some active compounds could not be dissolved by the solution and additional extraction should be deployed making the process more expensive and practically not applicable.

The frequently offered method for destruction in coke ovens is not applicable due to following reasons:

1. Temperature reached is not high enough for full thermal destruction of the pesticides.

2. One part of the pesticides could be vaporized and mixed with the row gas.

3. Due to the continued storage the active substance could be oxidized partially. This is typical for chlorine containing pesticides which could generate dioxins during the processing.

4. The method does not guarantee 100% destruction of the pesticides.

5. Control of the emissions for residues from pesticides and dioxins is not planned.

6. The mineral compounds endanger the brickwork with creation of slag and consequent damage to coke ovens.

7. The method is not supported with laboratory and experimental results for proof of efficiency to guarantee the utilization of pesticides.

All these problems make the method not applicable.

In the last three months of 2003 with the funding from the Standing Committee for Protection of Population in Case of Disasters and Accidents the full inventory of the storehouses with pesticides was accomplished. The facts show that the private sector has problems with storage of pesticides too. This shows the need for amendments in the current legislation and adoption of new acts to guarantee (not without the interference of Ministry of Environment and Water) environmental safe storage of pesticides. It is important also to emphasize on the question for construction of depots for such wastes (other organic wastes are not excluded) as well as installation for destruction of such kind of substances.

Aiming to ensure safety for the population, full inventory of objects storing pesticides should be accomplished. Thus the risk under defined conditions – floods, fire and other disasters could seriously pollute the environment and endanger the population in neighboring areas could be assessed.

ANNEX I: LIST OF PARTICIPANTS

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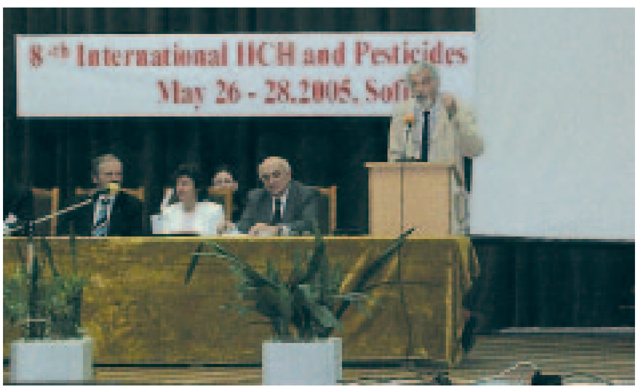
ANNEX III: PHOTOS

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