HCH CONTAMINATION IN THE SABIÑANIGOS´S ENVIRONMENT (SPAIN)

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The manufacture of lindane between the years 1975 to 1988 in the city of Sabiñanigo, Aragonian Pyrenees (Spain), left away several sites contaminated by the dumping of solid wastes. About 80,000 tonnes of HCH mixture remain located at three main sites that lack of an adequate liner system.

At these sites, a DNAPL groundwater plume has been found, containing benzene, chlorobenzenes and chlorophenols and a mixture of HCH isomers. With a density of 1.5 cps and 950 g/kg of contaminants it constitute a serious risk due to the vicinity of the Gallego river and the complex aquifer system consisting in alternating verticals sandstones and marls.

Geographical location of the lindane contaminated sites

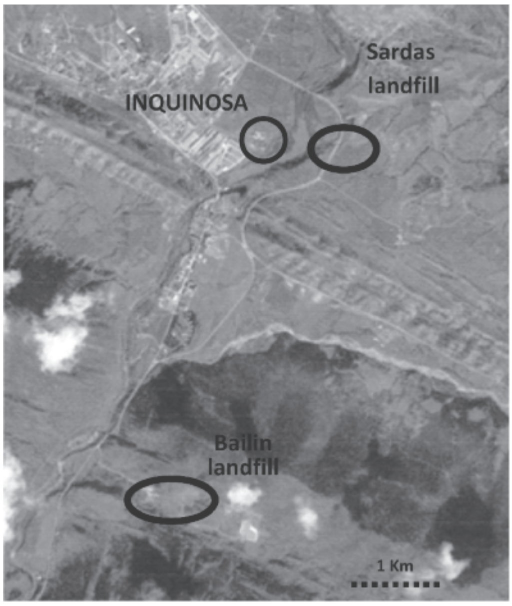
In the XX century, and until the closure of INQUINOSA at the end of the 80´s, bad environmental practices associated with the dumping of the solid waste generated in the city and his industries left away several contaminated sites.

The firm INQUINOSA produced lindane from 1975 to 1988, and formulate lindane products until 1992. Waste generation data differs upon the information source used: about 6,800 MT/year of solid waste and 300-500 MT/year of liquid waste (1,500 MT/year for other sources) were estimated.

The Regional Government and the Spanish Ministry of the Environment are taking action, focusing in the DNAPL treatment and, due to the high quantities involved, in the temporal confinement of the solid waste until proper disposal operations were develop.

Lindane containing solid waste in Sabiñanigo

Sabiñanigo is a small industrial city located in the Aragonian Pyrenees (Spain). At the beginning of the twentieth century bulk chemical industries were installed. In the seventies the factory of the firm INQUINOSA began to produce lindane.



Without taking account of small dumps sites, four sites remain contaminated: the Sardas and Bailin dumping sites, the industrial ruins of INQUINOSA, and the dam of Sabiñanigo. In the first three sites the Regional Government of Aragon is executing remediation works, while the dam is supervised by a national authority.

The dumping site of Sardas:

The Sardas site is located over Eocene marls, and lacks of a liner system in its basin. It contains about 350,000 m^3 of all kinds of solid wastes. The disposal of wastes generated at a chlorine production facility causes a lixiviates pH of 13. The wastes also contain high amounts of hydrocarbons, metals and lindane isomers. It is estimated that over 30.000 and 80.000 MT of dust HCH wastes and 2.000 Mt in, liquid form were disposed in this site.

In 2009, a DNAPL was detected in the surface. Immediately collection works and studies of the hydro-geological behavior of the site were initiated, as a work previous to consider viable confinement and treatment alternatives for its later implementation. This site is treated in other communication at this congress, and details are given there.

Inquinosa's industrial ruin

The production facility of INQUINOSA closed in 1994, removing operative equipment and remained abandoned. Now, after obtaining judicial access, soil and groundwater characterization and an inventory of the wastes found in the site, have been undertaken.

	SOIL				WATER			
Parameter	Unit	NGR	maximum	mean	Unidad	maximum	mean	minimum
Benzene	-	10.000	**60.000**	2.546	µg/l	120.000	37.633	1.800
Phenol	µg/kg ms	100.000	2.200	341	µg/l	310	139	13
Dichlorobenzenes	µg/kg ms	40.000	**247.300**	10.561	µg/l	8.200	2.535	<1
Trichlorobenzenes	µg/kg ms	90.000	**801.600**	38.162	µg/l	2.007	701	<1
Tetrachlorobenzenes	µg/kg ms	-	279.000	12.504	µg/l	245	93	<1
Pentachlorobenzene	µg/kg ms	-	20.000	955	µg/l	16	6	<0,1
Monohlorobenzene	µg/kg ms	35.000	**1.600.000**	**65.167**	µg/l	42.000	16.428	370
Chlorophenols	µg/kg ms	100.000	640	161	µg/l	77	22	<1
Dichlorophenols	µg/kg ms	10.000	1.900	308	µg/l	43	15	<1
Trichlorophenols	µg/kg ms	100.000	4.200	648	µg/l	123	34	<1
Pentachlorophenol	µg/kg ms	1.000	**3.200**	452	µg/l	3	1	<1
α-HCH	µg/kg ms	1.000	**57.000.000**	**2.303.197**	µg/l	2.000	730	21
β-HCH	µg/kg ms	1.000	**5.600.000**	**245.523**	µg/l	1.400	712	20
γ-HCH	µg/kg ms	1.000	**9.700.000**	**406.837**	µg/l	2.800	1.158	9
δ-HCH	µg/kg ms	-	2.200.000	105.722	µg/l	7.600	2.269	13
e-HCH	µg/kg ms	-	2.700.000	138.885	µg/l	1.400	640	31
Total- HCH	µg/kg ms	-	**74.730.000**	**3.200.165**	µg/l	15.000	5.509	94
NGR: maximum concentration acceptable for industrial land use in Spanish law								

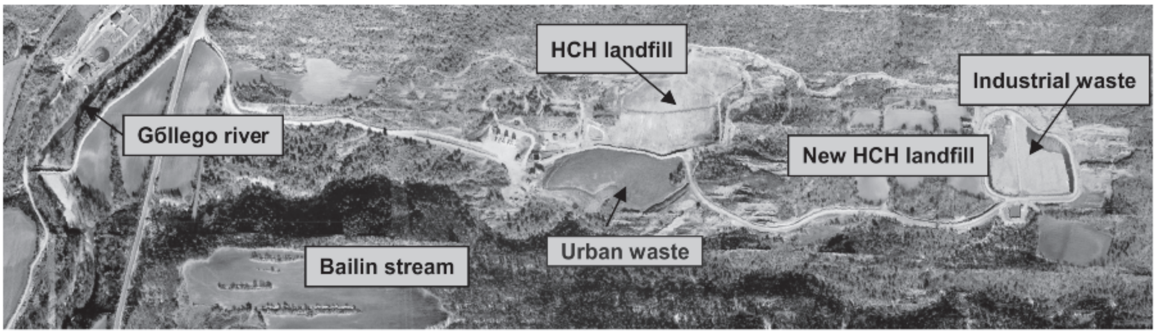
Table 1. Concentration of HCH and other chlorinated compounds in soil and groundwater in the INQUINOSA ruins

About 100 MT of HCH, 6 MT of o,o-dimethyl phosphorodithioic acid that was used in the manufacture of Phosmet insecticide, and other chemicals still remains in the industrial ruins.

Short-term interventions include legal declaration as a contaminated soil, characterization of the site and the solid wastes remaining, which in part were treated by an authorized agent, and in part were translated to a conditioned landfill in Bailín. Remediation of the site is conditioned by the judicial position of the property and in last instance by budget provisions at regional level.

The Bailin's dumping site

Between the 1984-1992 a site near de urban nucleus of Sabiñanigo was used for the disposal of industrial and municipal solid wastes. It is located over and alternating vertical series of sandstone and limolite strata, without liners in his basement. A final cover with a HDPE liner was made in 1996. The total volume of the landfill is 180,000 m^3, containing about 30,000 – 80,000 MT of HCH solid waste and 2,000 MT in liquid form.



Landfill sites at the Bailin creek.

The liquid form waste is a dense mixture of benzene, chlorobenzenes and chlorophenols, and HCH isomers, with a density of 1.5 cps and 950 g/kg of contaminants, behaving as dense non-aqueous phase liquid (DNAPL).

Parameter	Unit	Maximum	minimum	Parameter	Unit	Maximum	minimum
Viscosity at 25°	Cps	12,1	14,2	2,4,5 Trichlorophenol	g/Kg	1,18	0,9
Density	Kg/l	1,543	1,3662	2,4,6 Trichlorophenol	g/Kg	3,426	0,31
Water	g/Kg	9	2,2	Tetrachlorophenol	g/Kg	0,254	**
Benzene	g/Kg	11,16	9,4	Pentachlorobenzene	g/Kg	1,7	<0,025
Chlorobenzene	g/Kg	140	75,53	Tetrachlorociclohexenes	g/Kg	18,64	1,97
1,2-Dichlorobenzene	g/Kg	18,89	7,4	Pentachlorociclohexenes	g/Kg	130,69	74,3
1,3-Dichlorobenzene	g/Kg	4,93	2,2	Hexachlorohexadieno	g/Kg	65,1	<0,025
1,4-Dichlorobenzene	g/Kg	20,5	17,03	Hexachlorociclohexano	g/Kg	167,00	**
1,2,3 Trichlorobenzene	g/Kg	6,50	2,96	**a-HCH**	g/Kg	**60,92**	**48,3**
1,2,4 Trichlorobenzene	g/Kg	74,92	29,57	**b-HCH**	g/Kg	**1,91**	**<0,025**
1,3,5 Trichlorobenzene	g/Kg	0,31	<0,025	**g-HCH**	g/Kg	**148,86**	**134,00**
1,2,3,5 Tetrachlorobenzeneno	g/Kg	13,49	5,1	**d-HCH**	g/Kg	**129,05**	**102,2**
1,2,3,4 Tetrachlorobenzene	g/Kg	12,72	5,3	**e-HCH**	g/Kg	**35,90**	**21,43**
1,2,4,5 Tetrachlorobenzene	g/Kg	11,1	**	Other HCH isomers	g/Kg	39,97	**
Phenol	g/Kg	1,72	**	Heptachlorocicloexano	g/Kg	96,38	1,39
Chlorophenol	g/Kg	<0,025	**	Other HCH metabolites	g/Kg	148,85	136,1
2,4 Dichlorophenol	g/Kg	0,045	**				
2,6 Dichlorophenol	g/Kg	<0,025	**				

Table 2. DNAPL properties and composition.

This dense liquid has percolated from the dumping site towards the Gallego river, 800 meters away, through a fracture net in the rock substrate. The liquid flows through four vertical strata of sandstone connected by horizontal fractures in the limestones alternates.

The DNAPL plume location depends on de strata and his grade of fracture, with a maximum of 150 m length and 20-40 m deep. The aqueous plume has reached the Gallego River and peaks of 1 µg/l of HCH has been measured 0.5 km down the river, with average concentration of 0.57 µg/l. These levels drop under the detection limit 2.5 Km down the river, due to flow incremental from and Hydro power plant channel. Occasionally a level of 0.1 µg /l has been recorded. According to the Council Directive 2008/105/CE the HCH average limits is established in 0.02 µg/l, and 0.04 µg/l for maximum peaks.

The treatment strategy in this site is conditioned by the DNAPL presence. Detected in 2006, the priority has been to stop its flow and control contaminant levels in the aqueous phase. As a result of this early work, a flow control protocol has been established. The efforts are now focused in study how the aquifers behave. First, we have developed a conceptual model and then a mathematical one assimilating a low permeability porous multilayer fractured media (based in Modflow code). The model, that fits well with experimental data, was used to know the hydrogeological balance and to design pilot test.

The control of the aquifer is done with 150 piezometer and a pumping and wastewater treatment system. The DNAPL is extracted from the aquifer by a programmed pumped system that avoids the flow of the plume, while the wastes that remain in the dumping site as the source of pollution, were disposed. 17,000 liters have been extracted since 2006. At the same time, being the plume under control, two additional working lines have been executed: removal of the pollution source and the study and test of aquifer remediation techniques.

Several remediation techniques (MERK, ISCO, ISTD, SEAR, ISGS, zero-valent iron) have been tested at laboratory scale. In site pilot test with surfactants (SEAR) are in progress. The results of this his studies will be published in the future, but preliminary results show the difficulty of treatment associated to this complex soil-aquifer matrix.

In 2007, the Project of dismantling and transfer of the Bailin dumpling site was redacted. A near site, in the same valley, was the chosen site. Due to social and security matters other sites far away with better hydrogeological conditions were rejected.

The disposal of the solid wastes was also rejected for several reasons:

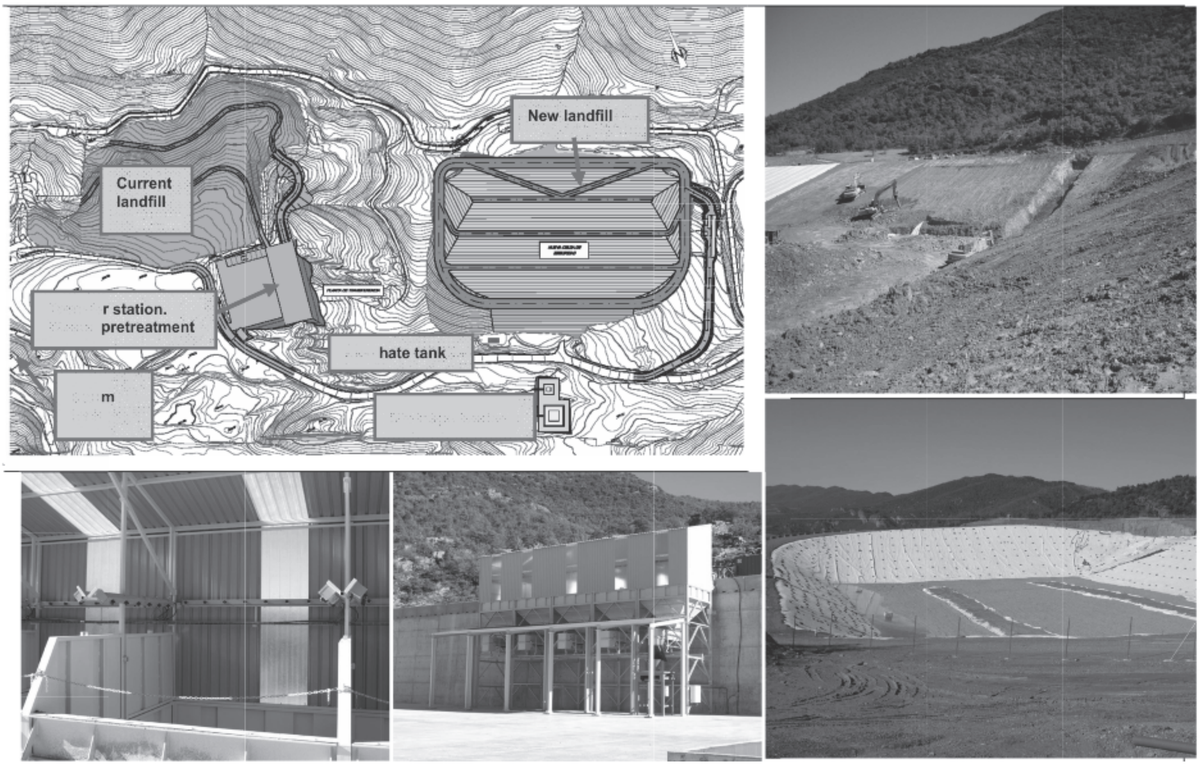
- The need to remove the source of pollution in short terms as a first step in order to proceed at the aquifer remediation.
- The limited yields of disposal techniques, being necessary several years to complete the treatment and also make necessary the transfer or storage of the wastes.
- The high quantities involved require proprietary pretreatment and disposal facilities, with associated high cost.

The Works began in 2010 with the construction of infrastructures to facilitate the dismantling.

Due to the inadequate geological characteristics of the site, the new cell has been constructed with isolating measures additional to the legal requirements. The landfill basin has a set of drainage trench 5 meter deep, excavating in the rock, to depress the water table. The waters collected were taken to a tank and his quality monitored prior to its released.

Over the rock, a compacted clay layer, a geo-drain and a gravel layer connected to a drainage system that divide the base and takes the flows to a control tank, isolate the landfill.

Two sets of geomembranes liners of HDPE (1.5 mm), bentonite (5,500 g/m^2), and HDPE (1.5 mm) impermeabilize the base. The sets are separated by a geo-drain in order to control possible leakages.



Infrastructures needed to dismantle the Bailin dumping site. Details of the transfer station. Chutes and dust suppression system. New landfill for the HCH solid wastes. Drainage system and final aspect of the new landfill cell.

A final gravel layer with drainage tubes collect the lixiviates, that are taken to a tank connected to the wastewater treatment plant.

The cap will consist in a gas collection system, a set of geomembrane liners of HDPE (1.5 mm), bentonite (5,500 g/m^2), and HDPE (1.5 mm), a geotextile, a geo-drain and soil.

The transfer station is designed to make the pretreatment of the solid wastes, depending on the size, the moisture content and the HCH concentration. It has four chutes, a packing system, a solidification-stabilization unit for high moisture content wastes, a centrifuge unit, a separator unit and a loading bay. A dust depressing system minimize the dust while operated.

The dismantling is planned for May-October 2012, coinciding with the low precipitation period. It will be executed advancing towards the laterals in layers of 2 meters deep. The operating area will be cover with a HDPE sheet with a dust depressing system in.

A grid of 30x30 m drilling test, sampling 2 m deep, will serve to characterize the solid wastes and to establish the pretreatment at the transfer station.

To minimize the risks associated to the transfer of the solid waste a meteorological system is available. The works will be suspended those days with rain and wind conditions.

The transfer to the new constructed landfill is not a definitive solution, but it will allow to take actions against the contaminated aquifer and it will provide a secure storage infrastructure until the development of adequate remediation techniques, maintaining costs and times at a reasonable level.

CONTAMINATION OF DRINKING WATER AND THE ENVIRONMENT BY THE PRODUCTION AND USE OF PFOS AND OTHER PERFLUOROALKYL COMPOUNDS (PFCs)

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Introduction

Polyfluoroalkyl compounds (PFCs) are very persistent, and several are toxic pollutants[1a,b]. In May 2009 PFOS and related substances were added to the Stockholm Convention POPs list[2]. Therefore, according to article 6 of the Convention PFOS contaminated sites should be identified[3].

PFCs are used extensively in numerous consumer goods (e.g. impregnated paper, textiles, leather, furniture), and eventually end up in landfills via disposal of these products. Due to their high water solubility, PFCs are subject to mobilization and release from landfills[4]. PFOS, PFOA, and other perfluorinated acids may be present in water in ionic and highly soluble forms, and water resources are a primary final sink due to the presence of PFCs in domestic wastewaters as well as certain industrial discharges.

The 3M Company was the primary global producer of PFOS-related PFCs, producing millions of pounds annually at its plants in the United States and Europe5. 3M produced PFOA at its Cottage Grove, MN/USA plant until the end of 2002 when it stopped production of PFOA and PFOS-related compounds. The production or use of other PFC-related compounds ("4 carbon PFCs") continues today[6]. Significant amounts of wastes, residuals, and sludges were generated in the production of PFCs and associated products. An assessment by the Minnesota Pollution Control Agency revealed that large amounts of PFC wastes from the 3M production plant in Cottage Grove, Minnesota, USA had been deposited in landfills and under the 3M production plant property[7].

PFC production also occurs in Europe with similar contamination. In this paper we briefly examine a European and a US contamination scenario related to PFC production: The 3M plant in Minnesota which resulted in contamination of the wider environment (groundwater, sediments, surface water, and fish)[7], and the contamination of agricultural land in Germany by application of PFOS/PFOA contaminated sludge imported from a European PFC production plant. This use of PFC contaminated sludge in Germany resulted in contamination of drinking water supplies to about 5 million people[13,14]. The cases both highlight the importance of the proper control, management and destruction of organofluorine production wastes.

Materials and Methods

Samples (soil, sediment, landfill leachates and gas condensate, ground water, sewage sludge and, fish) were collected by MPCA staff.[7] Soil cores were obtained by soil borings at the landfill site. PFC analysis (up to 14 different PFCs including PFOS and PFOA)[7] was performed by a commercial laboratory using approved standard methodologies. Analysis and quantification of PFC was performed by LC-MS/MS.

In the German case, analyses were carried out on an Agilent 1100 HPLC System interfaced to an API 2000 triple-quadrupole mass spectrometr. Analytical details are reported elsewhere[8].

Results and Discussion

1) The Minnesota Case

The Minnesota investigation of selected 3M PFC production sites and associated environmental contamination included.

Washington County Closed Landfill

The Washington County landfill (WCLF) is a 35 acre unlined closed landfill with no leachate management. After elevated VOC levels were found in groundwater below the site in 1981, a 'pump and treat' system was installed including a spray stripper system where contaminated groundwater was sprayed into the atmosphere to volatilize/remove VOCs. This system operated for about 25 years.

3M disposed of PFC production wastes to the landfill from 1969–1975. The study found high PFC contamination in the groundwater under and close to the landfill. PFCs migrating downgradient from the site caused extensive contamination of private drinking water wells. PFOA and PFOS concentrations in groundwater, at up to 42 ppb and 2.7 ppb respectively, exceeded the then drinking water criteria of 7.0 ppb and 1.0 ppb; the standards were subsequently reduced to 0.5 and 0.3 ppb, respectively[8].

"Ponded" stripper water was found to contain up to 1.7 ppb PFOS, 15 ppb PFOA, and 352 ppb PFBA. PFCs were found deep within the soil profile at the site – probably due to the spray stripping system and continuous PFC migration over 25 years of stripper operation. PFBA, as well as PFOA, was found to be highly mobile, moving many kilometers down-gradient in the groundwater. PFBA was found present in groundwater up to 1170 ppb. A drinking water criteria was later established for PFBA at 7.0 ppb, and the same value of 7.0 ppb is proposed for PFBS. Widespread PFC contamination in drinking water wells resulted in a program that in their replacement by alternate water supplies or the fitting of individual activated carbon water treatment systems. The Washington County Closed Landfill is currently being remediated with the installation of a composite-liner system with leachate collection.

Pine Bend Landfill (PBLF)

The Pine Bend Landfill PBLF received wastewater treatment plant sludges from the 3M production plant[7]. The PBLF has both lined and unlined areas. Leachates from the PBLF contained PFOA, PFOS, and PFHxA in leachate up to 82 ppb, 31 ppb, and 29 ppb, respectively, with total PFCs up to 178 ppb. PFCs were also detected in groundwater, with higher levels in downgradient wells (PFOS and PFOA at 0.11 and 1.6 ppb,respectively), indicating migration of PFCs from the landfill to groundwater.

Gas condensate generated from the landfill, normally collected and treated at the Twin Cities Minnesota main Metro wastewater treatment plant, was analyzed. This is the first study we are aware of where PFCs have been analyzed in landfill gas condensates. PFOA, PFOS, and PFHxA in gas condensate were found at unexpectedly high levels of 84 ppb, 30 ppb, and 38 ppb, respectively, with total PFCs up to 194 ppb. PFC levels in gas condensate suggests that PFCs could be released to the atmosphere through emission of landfill gases.

3M Wastewater Treatment Plant (WWTP)

3M has discharged treated PFC production wastewaters to the Mississippi River since about 1950. These wastewaters are treated using a conventional activated sludge system and an activated carbon filtration system was added to the system in 2004. 3M data for PFC concentrations in the wastewater discharge prior to the termination of PFC production in 2002 was used by MPCA staff who calculated that 33,000 kg per year of PFCs could have been discharged to the Mississippi River[12].

In 2005 it was found that the total concentration of the 13 PFCs in the 3M WWTP final effluent to the river was 291,300 ppt. PFOS and PFOA levels were 19,200 and 62,400 ppt, respectively. The highest PFC concentrations in the effluent were PFBA and PFBS at 80,600 and 104,000 ppt, respectively. PFOS and PFOA increased in concentration through the WWTP activated sludge system, probably due to the biological degradation of PFOS and PFOA precursors. Preliminary analysis indicated that the activated carbon system was relatively efficient and removed about 95% of PFOS but only 79% of carboxylic PFCs and 42% of PFBA. Whilst discharge data prior to the stopping of PFOA and PFOS-related production in 2002 is limited there are indications that much greater levels of PFOS have been discharged to the river in the past. In Jan-Mar 2001 and Sept-Oct 2001 the average PFOS discharged was about 1,403,000 ppt and 262,000 ppt, respectively, and 550,000 ppt in Dec. 2002[9].

The 3M plant non-contact cooling water also contained PFCs totaling 30,460 ppt. Cooling water is comprised of groundwater pumped from a barrier well system at another closed unlined landfill nearby (3M Woodbury Landfill) where PFC production wastes were disposed in the past.

Mississippi River Water, Sediment, and Fish

PFCs were analyzed in Mississippi river water, sediment, and fish near and downstream of the 3M plant and wastewater treatment plant discharges. PFOS was detected at 6 and 15 ppt in the river downstream of the plant. PFOA was found at 35 ppt downstream. The surface water from a cove area that immediately receives the PFC plant wastewater discharge contained PFOS, PFOA, PFHxS, and PFBS up to 18,200 ppt, 3,600 ppt, 9,700 ppt, and 89,800 ppt, respectively.

PFCs in the top 10 cm of sediment cores of the river and cove were also analyzed. PFOS levels were at 1.6 ng/g in a sediment core upstream of the plant, and 27.9, 8.3, and 1.7 ng/g in cores downstream of the plant. PFOS in the cove sediment core was 99 ng/g with total PFCs at 188 ng/g. A significant mass of PFOS in the cove sediment may pose a reservoir for PFOS exposure to benthic organisms and fish.

Fish tissue (fillets), blood, and livers were analyzed to determine whether fish PFC levels represented a source of risk for human consumption. Fish were collected from two areas in the Mississippi River near and downstream of 3M plant in August 2004, and October 2005. Elevated levels of PFOS were found in fish, with 40 of 42 fish (fillets) exceeding a Minnesota Department of Health (MDH) guideline that triggered a fish consumption advisory at 40 ng/g. Elevated PFOS levels were found in liver and fish blood. The PFOS level in the blood of one, year old, White Bass was 29,600 ng/g. We believe this to be the highest PFOS level found in any animal worldwide. PFOS in fish collected farther downstream of the PFC plant contained lower levels of PFOS, but still exceeded fish consumption guidelines.

2) A German Experience

In 2006 Skutlarek et al.[13] reported on perfluorinated surfactant contamination of the German river Ruhr (up to 446 ng/l), the tributary river Möhne (up to 4385 ng/l) and in tributary creeks (up to 43,000 ng/l). PFOA was/ is the main contaminant accounting in most cases for ca 80% of the PFC. The drinking water in this area, which serves approx. 5 million people, was contaminated with PFS up to 598 ng/l (PFOA 519 ng/l) in the most affected area.13,14 Some agricultural fields on the upper reaches of the Möhne river were identified as a main emission source.[13,14]

The PFOS/PFOA contaminated sites on the agricultural fields resulted from the mismanagement of PFC containing sludge which was imported by a German company from The Netherlands in accordance with the EU Waste Shipment Regulation for hazardous waste (EEC 259/93). In a criminal act the company declared the sludge as bio-waste and sold it to farmers. In September 2006 the BUND (FoE Germany) accused the company and also the local authority Soest[14]. The company proclaimed bankruptcy after the contamination was revealed and the former owner and CEO of the company went to prison. The comparison of PFC surface and drinking water contamination showed that the PFC were not reduced sufficiently by most water works (Table 1). Higher levels of reduction could be seen only for a few water works with high ground water dilution levels or by using new activated carbon (Table 1). The observed correlation of the PFC concentrations in surface water and drinking waters indicate that even water treatment works in industrialized countries do not effectively eliminate PFCs, although approximately 50% of the waterworks were equipped with activated carbon filters. The population in the area with the highest drinking water contamination (approx. 500 ng/l PFOA in March 2006, table 1) increased their PFOA levels in blood plasma by five to eight times compared with German background cohorts[15] after only ca. 3 years exposure (children 4.5-fold (median 22.1 µg/l), men 4.7-fold (median 27.4 µg/l) and mother 8.4-fold (24.9 µg/l)). The maximum values, in two children were 383 and 218µg/l. Considering of the bioaccumulation potential of PFC and the alarming health effects reported including reduced birth weight of infants and reduced sperm quality[16], these human levels indicate that the proposed German drinking water guidelines are too high.

Table 1. PFC concentration in surface waters and related drinking waters of some cities in the Ruhr area

	PFOA [ng/L]		Sum of PS [ng/L]	
City:	Surface water	Drinking water	Surface water	Drinking water
Mülhelm	48	31	94	63
Essen	60	58	97	104
Bochum	58	53	91	96
Witten	75	50	147	91
Hagen	91	65	152	118
Schwert	178	146	280	234
Neheim	646	520	765	609

Several water treatment works in the region were upgraded at a cost of approximately 100 million EURO. The agricultural use of PF contaminated areas is now controlled and recommendations have been given for the human consumption of contaminated fish.

Conclusions

This study illustrates that PFCs deposited and released at landfills or from contaminated agricultural areas are highly mobile and contaminated the wider environment. Substance flows from landfill leachates to wastewater plants and rivers, from landfills to groundwater, from landfill gases to atmosphere, and from contaminated ground water sprayed to the atmosphere, reveal multiple pathways for PFCs at landfills and disposal sites to end up in surface waters and fish. Human exposure and risk assessments around such contaminated sites including all exposure pathways such as fish consumption, drinking water intake, soil ingestion, fruit and vegetable consumption, and possibly even intake via inhalation of air and landfill gas emissions near those sites, should be performed to assure adequate safeguards.

The German case demonstrates that mismanagement of waste streams from PFC-producers can contaminate the drinking water of millions of people. In addition to the immediate contamination of sites around PFC production plants, waste streams of these industries can become a significant hazard to humans. Therefore, the mass flow and waste management of PFC producing and using industries should be tightly regulated by national authorities.

The German and the US case show that even relatively well regulated countries with established hazardous waste management regimes have considerable difficulty in controlling these contaminants. Consideration should be given to how developing and transition countries can ever effectively regulate and control PFC production and use or the disposal of contaminated products. Countries need to be aware of PFC wastes and waste streams including those in consumer products and the need to manage and destroyed them in an environmentally sound manner. Compliance with the obligations of the Stockholm Convention is essential if countries are to effectively address PFC contamination.

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Disclaimer –The Minnesota data used in this study/report was acquired during MPCA studies while two of the authors were MPCA staff. The MPCA was not involved with preparing this paper.

SESSION 3. EXPERIENCES WITH OBSOLETE PESTICIDES AND POPS IN AZERBAIJAN

MANAGEMENT OF OBSOLETE PESTICIDES IN AZERBAIJAN

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Abstract

The data about production, use and storage of pesticides in Azerbaijan for the last 60 years are reported. Azerbaijan had a developed agriculture in the Soviet era. Up to 60 thousands tonnes of pesticides per year were used in pest control of the agriculture. A part of these pesticides was produced in Sumgait chemical complex and a part was imported from outside. During 1951-1978, the Sumgait factory of Surface-active-substances produced 480,549 tonnes of 5 % DDT. For this purpose, 25 thousands tonnes of pure DDT was imported from Russia. The data about production and usage of DDT in Azerbaijan in 1958-1980 are provided in this paper. It has been recorded that 283,827 tonnes of DDT was used in the cotton-growing areas of 24 regions of Azerbaijan. Data about production of hexachloran in 1951-1978 and lindane in 1986-1988 are also provided. Information about "hot spots" and environmental impact of obsolete pesticide are also provided. After 2004 the Government of Azerbaijan took steps to deal with the obsolete pesticides in the country. The results of the first inventory and monitoring of the obsolete pesticides within the framework of the projects of the Ecological Society "Ruzgar", financed by the International POPs elimination Network (IPEN) and Caspian Environmental program are reported in this paper.

Key words: Pesticides, production, use, "hot spots", capacity, NGO.

Introduction

According to FAO every year 34 % of the world potential crops – with estimated cost of 75 bln US dollars - are destroyed by insect pests and weeds. The 50% of these losses are happening in the countries, which tend to lag behind the economic development. It is impossible to receive high and stable crops in the agriculture without the application of pesticides. These chemicals are applied to protect the plants from insect pests and diseases, and also to fight against weeds. The excessive use of pesticides without consideration of application instructions application instructions lead to environmental contamination and negative health impact. During Former Soviet Union (FSU), the centralised management system of agriculture used to overlook the use of pesticides above permissible amounts, that resulted in the vast pollution of soil, water and air. It is necessary to note that the majority of pesticides used were persistent and stable in the environment.

In the 1970s and 1980s, 1.4 million tonnes of grain, up to 700-800 thousand tonnes of cotton, over 1 million tonnes of grapes, more than 1.2 million tonnes of vegetables, 400 thousand tonnes of fruit and other agricultural products were produced in Azerbaijan. At the same time, the climate of Azerbaijan was very conducive to the distribution of various diseases by insects and pests of agricultral products. After the break up of the Former Soviet Union (FSU) the use of pesticides has decreased 20-fold. However, the accumulated unused and banned pesticides still represent threat to the environment and health of the population.

1. Production of pesticides in Azerbaijan

During 1984-1994, nearly 20 thousand tonnes of surface-active substances were produced in Sumgait factory. The factory was established in 1958 to produce DDT with a capacity of 60 thousand tonnes a year. The production proceeded until 1980. Within 22 years of production, the technical dust containing 4.5-5% of DDT had reached 482539 tonnes. It is worth to mention that production of DDT was banned in the FSU in 1970. In 1951 the factory of surface-active substances began to produce technical hexachloran containing gamma-isomer hexachlorcyclohexane (lindane), and within 27 years produced 30,449 tonnes of hexachlorcyclohexane. The process was built on the basis of photochemical chlorination of benzene. In 1986-1989 the same factory produced 181 tonnes pure gamma-isomer hexachlorcyclohexane - lindane, that was sent to Novomoskovsk (Russia). Today “Preparation - 30” is the only plant protection product produced in Azerbaijan. This pesticide is used as a winter treatment in the orchards and vineyards.

2. Use of pesticides in Azerbaijan

81 pesticides and chemicals were introduced to the Azerbaijani agriculture to protect the crops. As an example data from 1989 are listed in Table 1 below:

Name of Pesticides	Quantity	Name of Pesticides	Quantity	Name of Pesticides	Quantity
BI -58, 40 %	3478	Nitrofen	800.9	Treflan 24%	15.9
Hexochloran 12%	1542.4	Preparat – 30	1668.1	Triallat 40%	12.6
Nemasid mixture	563.4	Benzophosphat	35.1	Propaxlor 65%	3.9
Metaldehid	154.9	Phazalon 60%	284.5	Simazin 80%	1.4
Copper sulfate	5802.9	Fozapan 25%	340.6	Utap 26%	7.4
Sineb, 80%	1236.7	Vofatox	113.8	Formalin	0.7
Copprozan 90%	652.2	Metafos 40%	668.2	Mineral oils	0.9
Polycarbosin 80%	90.1	Karbofos	26.9	Tigan 70%	216.6
Polykam 80%	58.5	Endosulfin	0.2	Gropazan 2%	25.2
Rydomil 25%	8.9	Tiodan 35%	16.1	TMTO	57
Tuberid 80%	5	Tiodan 50%	77.5	Trifolin	21.4
Tint 20 %, kg	4.5	Sumisidin 20%	79.5	Zinc pholisphid	23.5
Arsarid 80%	112.2	Fenvoderaq 20%	4	Cotton shprat	511.2
Phundozon 50%	27.1	Medin 20%	6.9	Shbberamin, kg	2.3
Banmethhon 25%	11.3	Pliktran 25%	17.8	Shbberesib, kg	3.5
Brimstone	15208.5	Dmayt 57%	37.1	Tur	69.1
Colloid sulfur	331.7	Polikaritoks 50%	16.8	Bitoksibasilin	29
Sulfur 80%	680.9	Dechish 25%	138.3	Dendrobasilimin	42.4
Karatan 25%	2.1	Nurel 20%	33.2	Magnum chromate	3029
Natrium proipiant	458	Sinibush 20%	9.4	Prometrin	1.5
Txan	39.9	Trichlorfon 80%	573.2	Sheril	0.8
2,4 – Diamine salt	634.1	Chlorophos 80%	104.6	Vitavax	3.3
Alirox 80%	59.8	Izophen 50%	105.7	Antio 22,5%	3.8
Eradiken	3.6	Aetelimoc 25%	0.7	Carate 5%	55.2
Dakmal	1.9	Keltan 20%	287.1	Rinkord 45%	0.3
Zenkf 70%	0.1	Abzilat 25%	0.5	Drop 50%	3
Dnok	418.9	Semeron 25%	0.2	Magnums chromate	3029

Table 1. Quantity (tone) of pesticides and poisonous chemicals used in Azerbaijan in 1989 categorised by their type

The distribution of DDT by regions in the cotton planting of Azerbaijan are listed in Table 2.

Region	*DDT*	*Region*	*DDT*	*Region*	*DDT*
Agdash	11115	Imishli	14076	Salyan	26542
Agdam	8675	Yevlakh	12045	Tartar	13088
. -	7280	Kurdamir	12006	Udjar	7777
Agdjabedi	19127	Gekchay	8311	Fizuli	6865
Beylagan	18365	Geranboy	9379	Shamkir	8721
Bilasuvar	12632	Neftchala	8942	Jalilabad	2253
Barda	19367	Saatly	14923	Jabrail	2452
Zardab	7646	Sabirabad	28226	Nakhchivan AR	5164
Total, tonnes					**283827**

Table 2. Use of DDT (tone) in cotton planting in the regions of Azerbaijan for 1965-1982

It should be noted that during 1984-2004 the quantity of used pesticides in the country decreased from 6705 t/year to 2720 t/ year. In 1991-2004 the registration and inventory of obsolete pesticides in Azerbaijan was not kept. The data on storage warehouses and usage of these obsolete pesticides were not available. There were the cases when population accessed pesticide containers and used obsolete pesticides in private farming.

3. ”Hot spots” of obsolete pesticides in Azerbaijan

IPEN framework projects created to make public-environmental inventory show that ”hot spots” can be divided into the following groups:

3.1. Places of pesticide production

Of concern in Azerbaijan is Sumgait factory of surface-active substances, which still contains DDT waste and other pesticides.

3.2. Polygons for storage of obsolete pesticides

The first inventory of obsolete and banned pesticides stored in polygon took place in 2004. The construction of polygon at distance of 53 km from Baku in Gobustan region began in 1963 and completed in 1990. As shown in the official data, nearly 8 thousands tonnes of obsolete and banned pesticides, mainly DDT, hexachlorcyclohexane, calcium-cyanamid, calcium-arsenad, were delivered in polygons in the years 1989-1991. Until 2006 the local population started to use the pesticides in their own agricultural facilities or for sale. After 2007 the polygon was reconstructed and protected in accordance with the sanitary-technical norms. From that time onwards, obsolete pesticides from other hotspot had been brought and stored at the polygon. There is also a Polygon for hazardous waste, where the obsolete pesticides from Dayikend are delivered.

3.3. Interregional bases of maintenance with chemical compounds

Until its abolition in 1996, the interregional chemicals storage warehouses were controlled by organization “Azselkhozkhimiya”. Afterwards the Open Joint-stock company “Azerkendkhimiya” took over the warehouses. They were privatized, and all the pesticides contained there were discarded. Some pesticides still contain obsolete pesticides that create risk to the environment. In total, there were 11 warehouses and 50 distribution points in Azerbaijan, some of which are closae to railway stations.

3.4. Former storehouses in former collective farms and field camps

It is true to say that pesticide warehouses existed in almost all cotton-growing collective farms and state farms. After privatization of the land, these points were liquidated and the rest of pesticides disseminated in the environment.
However, the number, characteristics and the exact site of all the storehouses have not been identified yet.

4. Distribution of DDT and Lindane in the soil and water environment of Azerbaijan

4.1. DDT and lindane in the soil of Azerbaijan

Since 1983, the Ministry of Ecology and Natural Resources of Azerbaijan has conducted monitoring of the level of DDT and hexachlorane in the soil from more than 10 stations. Within a period 22 years, a huge analytical material has been collected, which made it possible to make a conclusion about changes of distribution and pesticide levels in the regions of Azerbaijan.
The territory of Azerbaijan can be nominally divided into 4 distinct areas such as:

1. Relatively clean areas where DDT and hexachlorane concentration is < 1 μg/kg
2. Areas with 1 μg/kg $<$DDT $<$10 μg/kg
3. Contaminated areas where DDT and lindane concentration used to be 15-20 times higher than the permissible concentration, and where the DDT and hexachlorane concentration today is 10 times lower than the permissible concentration
4. “Hot spots” where DDT and hexachlorane concentration can reach several percent.

However, this division of territory should be used with caution as regular and consequtive analyses on all territory have not been done yet.

4.2. DDT and lindane in potable water of Azerbaijan

About 70 % of the Azerbaijani population use the resources of the transboundary rivers of Kur and Araz for drinking water and irrigation. Therefore the measurement of the concentration of pesticide levels of Kura waters has been of great importance. The Company "Azekolab" has measured the content of DDT and lindane in 4 points of the rivers Kura and Araz. The concentration of DDT and lindane in Kura and Araz waters and in suspense particles, was much below the permissible norm and, in many cases, even below the sensitivity limit. The reason is the sedimentation of firm particles in cascade water reservoirs of the Shamkir-Yenikend-Mingechevir-Varvara, but it is also possible that the measurements are low due to the small probability of penetration of pesticides in superficial waters at the distance Mingechevir-Shirvan.

5. Capacity of the Republic of Azerbaijan on management of pesticides

5.1. Capacity at the systemic level

Azerbaijan has signed the Basel and Stockholm Conventions and carries out corresponding obligations. National Legislative basis of management of pesticides consists of the law of the Republic of Azerbaijan on "Phytosanitary control" from 2006 and the legal acts on realization of the main law. For the last 10 years, the Government had adopted various National and State Programs, which include problem of management of obsolete pesticides:
The State Program on Poverty Reduction and Sustainable Development (2008-2015); The National Program for Ecologically Sustainable Social-economic Development (2003); The State Strategy of the Azerbaijan Republic on Management of Dangerous Wastes (2004); The Program on Social and Economic Development of Regions (2004); The Program of Development of Agrarian Sector (2008), etc.

5.2. Capacity at the Institutional level

The main Stakeholders at the institutional level: The Ministry of Ecology and Natural resources, The Ministry of Agriculture, The Ministry of Health, The Ministry of Emergency, The Ministry of Justice, Milli Medjlis (Parliament), The Customs Committee, The Statistics Committee, the local executive authorities and municipalities, NGOs, and Mass-media.

5.3. The international organizations

Various programs of the United Nations (UNIDO, UNDP, UNOPS), FAO, WB, IREN, CEP) finance the international projects on POPs management in Azerbaijan, which are carried out by the Governmental Agencies and NGOs.

With support from the UNIDO program, in 2005-2006, The Ministry of Ecology and Natural Resources carried out the project entitled as "Development of the National Implementation Plan on Stockholm Convention". The process of creating the National Implementation Plan (NIP) involves all stakeholders. At present, the MENR, Ministry Agriculture and Ministry Health are working on projects covering various aspects of management of POPs and pesticides.

5.4. Participation of the NGOs in the management of the obsolete pesticides

The Ecological Society "Ruzgar", financed and methodically supported by IPEP, the Center of "Ecoaccord" and the Caspian Ecological Program have developed about 10 projects on inventory of the obsolete pesticides, monitoring of these substances in the environment and public awareness of this problem. "Ruzgar" is also involved in a project initiated by the World Bank on inventory of POPs in Azerbaijan and Caspian POPs Workshop in Baku on 2009. Further, the Ecological Information Agency ECORES also implement projects on management of pesticides, and public awareness.

5.5. Private Companies

There are more than 12 private companies, which deliver pesticides and chemicals for use in the agriculture in Azerbaijan.

6. NGO-proposals on improvement of process to manage pesticides

By their performance of obligations under the Stockholm Convention in Azerbaijan the NGOs came up with the following suggestions:

- Improve the National legislative and

normative documents according to the European Directives

- Create a special Center for management of the obsolete pesticides in Azerbaijan, which can organize and coordinate activities between various Agencies
- Deepen the activities on inventory of the obsolete pesticides in the country;
- Allocate special bunkers in the polygon for separate classes of the POPs
- Package and repackage obsolete pesticides and transport them to the polygon
- Conduct large-scale information campaign on the management of obsolete pesticides
- Develop and provide awareness of population for re-collection of DDT, hexachlorane and other dangerous pesticides from population.

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QUANTUM CHEMICAL CALCULATION OF ELECTRON STRUCTURE OF THE TETRACHLORINATED DIBENZO-PARA-DIOXIN ON THE BASIS OF SLATER-TYPE ATOMIC ORBITALS

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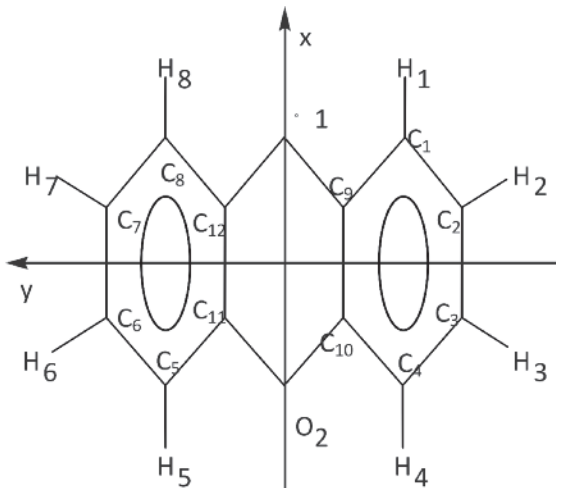
The paper reports on the results of quantum-chemical calculations of electronic structure of 22 isomers of tetrachloro-dibezo-para-dioxin using Wolfsberg-Helmholtz method (W-H method).

Continuing our research on calculation of atomic charges in the molecules of mono-, di-, and three chlorinated dibenzo-para-dioxins, [1,2] to establish correlation between the number and the location of chlorine atoms in phenyl rings and the toxicity of the molecule [3], in this work we study the electronic structure of 22 isomers if tetra-chlorine-substituted molecules of dioxin using Wolfsberg-Helmholtz method (W-H method).



The molecule of dioxin $C_{12}H_xO_2$ consists of 22 atoms as shown in Figure 1. The tetra chlorinated isomers are derived by simultaneous substitution of 4 atoms of hydrogen to 4 atoms of chlrorine. It's known, that in this way tetrachloro-dibezo-para-dioxin produce 22 isomers.

The Wolfsberg-Helmholtz method is one of the semi-empirical ways of Molecular Orbital (MO) theory of Linear Combination of Atomic Orbitals (MO LCAO). The molecular orbitals describe the status of electrons in a molecule, and are represented as a linear combination of atomic orbitals in the molecule of interest:

$$U_i = \sum_q Cq_i X_q \qquad (1)$$

where, X_q is a basis atom orbital.

For basic functions, we use real Slater-type atomic orbitals (SAO) [4]:

$$Xq \equiv X_{nim}\left(\xi, \bar{r}\right) = \frac{(2\xi)^{n+1/2}}{\sqrt{(2n)!}} r^{n-1} e^{-\xi_r} S_{lm}\left(\theta,\varphi\right), \qquad (2)$$

where $S_{lm}\left(\theta,\varphi\right)$, is real spherical harmonics.

$$\xi_i = \frac{z-y_i}{n} \qquad (3)$$

For determination of exponential parameter ξ we use the followings formula [5]:

$$\sum_{j\neq i}^{N}\left\{1+\left(\frac{3n_j^2-l_j\left(l_j+1\right)}{3n_j^2-l_j\left(l_j+1\right)}\right)^2\right\}^{-3/2} \qquad (4)$$

where N= number of electrons in the atom.

The quantum mechanical calculations of electronic structure of a molecule are restricted to the valence electrons of atoms, and the molecular orbitals are represented as a linear combinations of SAO of the valency electrons. For each of carbon and oxygen atom valance SAO are 2s-, $2p_x$-, $2p_y$- and $2p_z$-, for hydrogen atoms 1s- and for chlorine atoms 3s-, $3p_x$-, $3p_y$- and $3p_z$ - Slater functions, respectively. Hence, in quantum mechanical calculations of tetra chlorinated molecules of dioxin (C12H4Cl4O2) as basis atomic orbitals we used 76 (12x4+4x1+4x4+2x4=76) Slater functions $\chi_{nlm}(\xi, \bar{r})$ of atoms of carbon, hydrogen, chlorine and oxygen. Applying formulas (2), (3) and (4) we determined analytical expressions of SAO.

In (1), C_{qi} – unknown coefficients, which are determined by solution of the followings system of equations of simple order of MO LCAO:

$$\sum_q \left(H_{pq} - E_i S_{pq}\right) C_{qi} = 0, \qquad (5)$$

where, the followings are included

$$H_{pq} = \int X_p \hat{H} X_q \, dV \qquad (6)$$

$$S_{pq} = \int X_p X_q dV \qquad (7)$$

Quantities of H_{pq} represent the matrix elements of effective operator of Hamilton for one electron, moving in a certain effective field, independent from other electrons; quantities S_{pq} are integrals of overlap between SAO X_p and X_q.

Therefore, for the solution of the system of equations (6). i.e. for determination of orbital energies ε_i and of corresponding set of coefficients C_{qi}, it is necessary to know the numerical values of H_{pq} and S_{pq}.

However, quantities H_{pq} cannot be accurately calculated, because real expression of $\hat{H}$ is unknown. Therefore, H_{pq} can be calculated in a variety of ways, one of which is a quantum-mechanical semi-empirical method of Wolfsberg-Helmholtz. According to this method, each diagonal matrix element H_{qq} is assumed equal to ionisation potential of the corresponding valence state of the particular atom, and not diagonal matrix elements are determined based on equation [6,7]:

$$H_{pq} = 0.5k\, S_{pq}(H_{pp} + H_{qq}), \qquad (8)$$

where the value of the coefficient is determined theoretically or from a comparison with the experimental data.

Its noteworthy, that for the quantum mechanical calculations of molecules in accordance with W-H method, it is required to find out the exact numerical values of integrals of overlapping (8) in the total coordinate system of the molecule. For this purpose, we use the analytical expressions obtained in [8-10]. For computational quantifications based on these equations, the Cartesian coordinates of the atoms in a molecule coordinate system are used.

In our calculations, we consider the dioxin molecule is planar, and in each case the centre of the Cartesian coordinate system is assumed to be the centre of the molecule mass. Z-axis is perpendicular to the projection of the molecule. For determination of the atom coordinates in each molecule, we used the following geometrical parameters (bond lengths and bond angles) [11]:

$d_{c\text{-}c}$= 1.4 *A*, $d_{c\text{-}0}$= 1.44 *A*,
$d_{c\text{-}h}$= 1.09 *A*, $d_{c\text{-}cl}$= 1.7 *A*
$<_{ccc} = 120^o$, $<_{cco} = 123^o$, $<_{coc} = 114^o$,
$<_{cch} = 120^o$, $<_{cccl} = 120^o$

Using these data, we have calculated the Cartesian coordinates of atoms for each isomer of $C_{12}H_4Cl_4O_2$. For determination of diagonal matrix elements H_{qq} of operator $\hat{H}$ we used the following values of ionization potential of valence state of the atoms of H, C, O and Cl [12]

(1s |H| 1s) = - 0.499786
(2s |C| 2s) = - 0.772096
(2p |C| 2p) = - 0.419161
(2s |O| 2s) = - 1.325536
(2p |O| 2p) = - 0.680952
(3s |Cl| 3s) = - 0.552337
(3p |Cl 3p) = - 0.882774

The effective charge of the atom A in molecule is determined according to MO LCAO formula [13]

$$q_A = n_A^o - \sum_i n_i \sum_{q \in A} |c_{qi}|^2 , \qquad (9)$$

where n^o_A is the positive nuclear charge of the atom *A* (for carbon n^o_C= 4, for hydrogen n^o_H = 1, for chlorine n^o_{Cl}=7, and for oxygen n^o_O =6), n_i is the number of electrons on *i*-molecular orbital. Summarising *I* is done using molecular orbitals occupied by electrons.

The program we developed for computer calculations using W-H method on the basis of

SAO allows to calculate the values of electron energy (E), the ionization potential (J), the coefficients in (1), and the effective charges (q_A) of atoms. However, in Table 1, for the studied molecules, we report only the numeric values of effective charges of atoms.

Dioxin $C_{12}H_8O_2$		1-Cl dioxin $C_{12}H_7O_2Cl$		2-Cl dioxin $C_{12}H_7O_2Cl$	
Atom, A	Effective charge, $_A$	Atom, A	Effective charge, $_A$	Atom, A	Effective charge, $_A$
C_1	0,908855	C_1	1,452762	C_1	0,906405
C_2	0,869797	C_2	0,862002	C_2	1,408271
C_3	0,869818	C_3	0,880951	C_3	0,865411
C_4	0,908618	C_4	0,884236	C_4	0,919351
C_5	0,908632	C_5	0,908701	C_5	0,908622
C_6	0,869950	C_6	0,869965	C_6	0,870058
C_7	0,870047	C_7	0,870131	C_7	0,870170
C_8	0,908799	C_8	0,908834	C_8	0,908807
C_9	1,577340	C_9	1,579158	C_9	1,587135
C_{10}	1,577284	C_{10}	1,583171	C_{10}	1,553161
C_{11}	1,577296	C_{11}	1,577677	C_{11}	1,577631
C_{12}	1,577199	C_{12}	1,578073	C_{12}	1,577121
H_1	0,299558	Cl	-0,574357	H_1	0,306369
H_2	0,290149	H_2	0,296708	Cl	-0,574729
H_3	0,290204	H_3	0,288828	H_3	0,296090
H_4	0,299541	H_4	0,299318	H_4	0,298270
H_5	0,299541	H_5	0,299540	H_5	0,299515
H_6	0,290640	H_6	0,290647	H_6	0,290646
H_7	0,290383	H_7	0,290382	H_7	0,290388
H_8	0,299548	H_8	0,299550	H_8	0,299521
O_1	-2,061644	O_1	-2,064557	O_1	-2,061253
O_2	-2,061338	O_2	-2,060763	O_2	-2,061605

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ULTRAHIGH RESOLUTION AND MULTIDIMENSIONAL ANALYSIS OF PESTICIDES AND COMPLEX SAMPLE MIXTURES WITH FOURIER TRANSFORM MASS SPECTROMETERS: ENHANCED IDENTIFICATION POINTS

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ABSTRACT

Various analytical approaches that utilize Fourier Transform Ion Cyclotron (FT-ICR) mass spectrometry and data reduction schemes for analysis of complex sample mixtures are discussed. Specifically, the advantages of high mass resolving power (MRP), mass measurement accuracy (MMA), and gas-phase ion-molecule reactions for highly confident identification of pesticides in complex sample mixtures such as contaminated soils, or water are demonstrated. High performance mass spectrometers (*e.g.*, FT-ICR MS or FTMS) combined with data reduction approaches allow rapid identification of chlorinated compounds including persistent organic pollutants (POP) and obsolete pesticides in complex environmental sample mixtures at the highest level of confidence currently achievable. This methodology avoids the need for a pre-separation step (*e.g.*, gas chromatography (GC) or high pressure liquid chromatography (HPLC)) and at the same time offers one of the most suitable approaches for highly reliable and rapid identification of contaminated areas at low concentrations (below femtomole range) and subsequent monitoring of the potential soil or water remediation processes.

INTRODUCTION

Our research is focused on various areas of "x-omics" and addressing issues related to sample complexities in biomedical and environmental research areas.[1-3] The term *"x-omics"* refers to a comprehensive study of various complex systems such as the components of a living organism (*e.g.*, genomics, metabolomics, proteomics, *etc*), an environmental sample, and/or a non-living system (*e.g.*, petroleumics).[3] In all of these research areas, we must resolve the different components of a mixture, determine individual molecular identities, acquire relative abundance or concentration information, and unravel potential interactions among the various constituents of the sample at a high level of confidence.

Ideally, for comprehensive characterization of a complex ensemble, we need to know **(a)** *types*, **(b)** *concentrations*, and **(c)** *nature of the interactions* of all individual components of the mixture under the investigation. For example, for detection of a potential pesticide in a heavily contaminated area, we must address a-c. *One of the most important initial steps in designing an implementation plan for remediation of a potentially contaminated soil or water ecosystem is comprehensive characterization of the environment at the molecular level*. Highly confident evaluation of the ecosystem under the study demands high accuracy and high precision and ideally identification of all molecular components that are present in these complex mixtures. Often it is not a difficult analytical task to inspect and characterize samples that contain only a few chemicals and at sufficiently high concentrations (depending on the detector response factor). However, with "real world" samples, such as contaminated soil or water, detection of analytes at low concentrations can present a formidable analytical challenge.

Conventionally, gas chromatography (GC) or other types of separation techniques (*e.g.*, high pressure liquid chromatography (HPLC)) are used in tandem with mass spectrometry to separate various analytes and subsequently detect each individual component present in the mixture. Although chromatography has been an excellent work horse to address sample complexities, the separation process requires additional time and often sample preparation steps. Here we discuss an analytical approach for detection of chlorinated contaminants (*e.g.*, persistent organic pollutants (POP), obsolete pesticides) present in complex environmental sample mixtures that avoids the need for prior sample separation.

Two dimensional (2D) graphical visualization techniques such as Kendrick plots can be used to simplify the interpretation and classification of different class compounds.[4] Highly confident characterization of pesticides in complex sample mixtures, such as soils contaminated with crude oil, requires multiple analyses and often high performance mass spectrometry (MS). For example, electrospray ionization (ESI) Fourier transform ion cyclotron resonance (FT-ICR) mass spectra of crude oil samples contain several peaks at each nominal mass and thousands of peaks in the entire mass spectrum.[5] Hence, characterization or classification of pesticides in such complex sample mixtures by conventional methods can be quite challenging or impossible.

For detection of dioxins and furans, a method that employs a GC in tandem with a high resolution sector mass spectrometer (*e.g.*,combined electrical and magnetic analyzers) can be used. We have shown that GC combined with high resolution MS can be used to differentiate gasoline samples from different gas stations for unambiguous source identification[6] as well as isomer differentiations.[7] Although these approaches provide invaluable information, they are not suitable for direct analysis of complex mixtures. Fernandez-Lima *et al* showed that the combined use of ultrahigh resolution MS and ion mobility spectrometry (IMS) provides unique fingerprinting ability in petroleumics.[8] Here, we discuss theoretical and experimental results for direct, rapid, and unambiguous identification of chlorinated compounds present in highly complex mixtures.

We utilize Kendrick plots and proton affinity (PA) differences (as an additional chemical dimension to Kendrick plots)[9] as well as multistage MS for analysis of complex mixtures at low concentrations. It is particularly important to note that "effective" concentrations of many of the chlorinated environmental contaminants can be increased via bioaccumulation and therefore an ideal detector must be sensitive enough to address these challenges. FT-ICR MS provides ultra high MRP and MMA and multidimensional analyses can be conducted using ion-molecule reactions. We could demonstrate that pesticide content of highly contaminated samples can be detected and visualized through data reduction and use of ultra high MRP and MMA. We selected oil samples from Naftalan (Azerbaijan) and deliberately inserted theoretical mass spectral peaks (corresponding to mass-to-charge (m/z) values of eleven chlorinated contaminants) in the acquired mass spectra. Here, we also use asphaltenes samples as examples of complex mixtures and show that pesticides and chlorinated chemicals can be differentiated visually and without a need for a separation step. Moreover, we discuss the merits of using additional identification points such as ultrahigh mass measurement accuracy (MMA) and ion-molecule reactions to enhance selectivity and reduce the probability of error.

EXPERIMENTAL

All of the chemical reagents and solvents were purchased from Sigma (Sigma, St. Louis, MO). An FT-ICR mass spectrometer equipped with an open-ended cylindrical Penning trap (IonSpec Corp., Irvine, CA) and a 9.4 tesla superconducting magnet (Cryomagnetics Inc., Oak Ridge, TN) was used to carry out gas-phase ion-molecule reactions and acquire mass spectra.[7] Ions were generated externally using an Analytica electrospray source (Analytica of Branford Inc., Branford, CT) equipped with an in-house built spraying setup. [1] Ubiquitin and substance P were used for external calibration of the mass spectra (Sigma, St. Louis, MO). Also an Orbitrap FTMS was used to acquire mass spectra of Asphaltenes extracts (toluene extracts) and samples that were deliberately spiked with chlorinated compounds. The list of halogenated compounds that were used for computer simulations (along with their chemical composition and molecular weights, columns two and three, respectively) are included in Table 1.

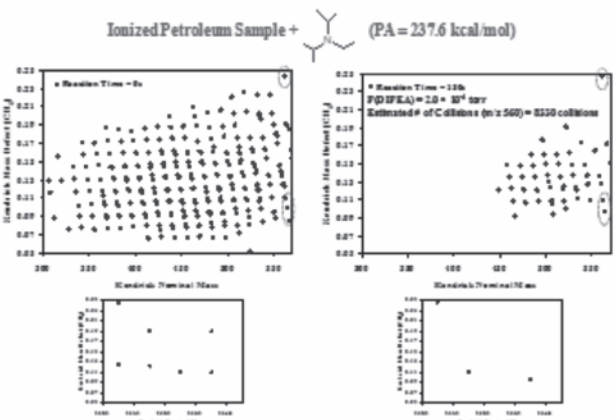
Table 1. Halogenated Chemical Compounds Used for Simulations

Compound	Chem. Comp.	MW
Lindane (γ-HCH)	$C_6H_6Cl_6$	287.86008
Norfluoxetine	$C_{16}H_{17}F_3ON$	297.13412
Sertraline	$C_{17}H_{17}Cl_2N$	306.08171
Fluoxetine	$C_{17}H_{19}F_3ON$	311.14978
4,4'-DDT	$C_{14}H_9Cl_5$	351.91472
Aldrin	$C_{12}H_8Cl_6$	361.87574
Heptachlor	$C_{10}H_5Cl_7$	369.8211
Endrin	$C_{12}H_8Cl_6O$	377.87065
α-Chlordane	$C_{10}H_6Cl_8$	405.79778
Miconazole	$C_{18}H_{14}Cl_4N_2O$	414.9939
Toxaphene	$C_{10}H_{22}Cl_8$	421.92306

RESULTS AND DISCUSSION

Figure 1 shows how identification points earned by MS can be increased by performing additional mass spectra (*e.g.*, acquiring tandem or high resolution mass spectra – please note that this Figure reiterates the original concept that was in introduced by Thurman *et al* earlier [10]). We have added mass measurement accuracy and ion-molecule reactions to indicate that these processes would increase earned identification points.[11] For example, we have shown that ion-molecule reactions and multidimensional MS can be used for isomer differentiation [12] and identification of halogenated disinfection byproducts (DBP).[9, 13] Ion-molecule reactions can also be used to reduce data complexity. To illustrate, in Figure 2, we show the Kendric plots for a portion of the m/z range for an oil sample from Nafthalan with diisopropylethylamine (DIPEA) (as a proton transfer reagent). Figure 2

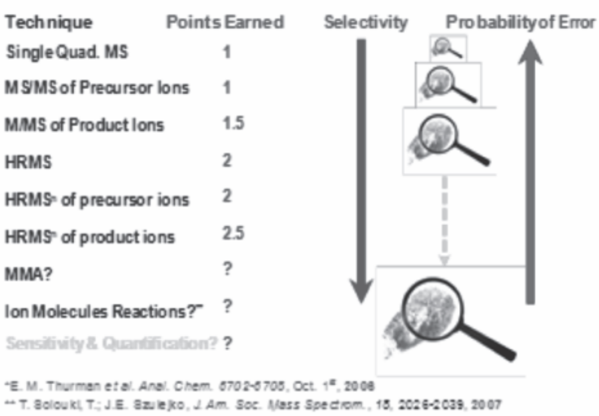
Figure 2. Proton Transfer Reaction



shows almost complete depletion of singly-charged ions from a typical crude oil sample (after 150 s reaction time at $P_{(DIPEA)} = 2.0 \times 10^{-6}$ torr). Detailed comparison of narrow mass range of Kendrick plots before and after reaction (for 150 s) with DIPEA shows selective depletion of chemical compounds with different chemical compositions. For example, among $C_{31}H_{61}O_2S_3$ (m/z 561.3828), $C_{40}H_{65}O$ (m/z 561.5030), $C_{36}H_{56}O_2N_3$ (m/z 562.4367), $C_{34}H_{66}O_2N_4$ (m/z = 562.5180), $C_{37}H_{58}O_3N$ (m/z 564.4411), and $C_{37}H_{72}OS$ (m/z 564.4298), only $C_{31}H_{61}O_2S_3$, $C_{34}H_{66}O_2N_4$, and $C_{37}H_{72}OS$ survive. These results suggest that the interpretation of Kendrick plots can be complemented by including PA as an additional dimension. Figure 2 shows that the complexity of data can be reduced by using appropriate proton transfer reagents. Such additional analysis dimensions can increase identification points which is a crucial parameter to consider for potential certification purposes (*e.g.*, agricultural products, petrochemical industry, xenobiotics analyses, *etc*).

Similar approaches can be used for identification of halogenated compounds in complex mixtures. Figure 3 contains a computer simulated (crude oil type) mass spectrum and its Kendrick plot on the left hand top and right hand top, respectively. In the bottom portion of Figure 3, computer simulated (crude oil type) mass spectrum and its

**Figure 1. Identification Points Earned by MS*
(inspection, verification, testing, and certification services)**



Kendrick plot of a spiked sample (with eleven halogenated compounds) are shown. Because of the mass deficiency for Cl atoms, a quick visual inspection allows rapid identification of all halogenated compounds (*viz.*, as expected, the halogenated compound with six Cl atoms or lindane (C_6 H_6Cl_6) shows the highest deviation in the simulated Kendric plot and is the easiest to spot from hundreds of interfering compounds in bottom right corner of Figure 3.

Our experimental results show similar trends where halogenated compounds stand out and can be visually identified. For example, Figure 4 depicts a FTMS mass spectrum (left hand side) and its Kendrick plot for toluene extract of an asphaltenes sample spiked with 1 ppb of miconazole (corresponding to less than picomole mass analyzed) after toluene extraction. Inset in Figure 4 show an expanded region for the m/z range 414.8 to 415.6 where more than fifteen peaks are present around the nominal mass of 415, with the halogenated species, miconazole, in the farthest left hand side with the lower m/z value (*i.e.*, peak corresponding to ions with the highest mass deficiency). A quick inspection of the Kendrick plots provides the same information and allows for rapid identification of all Cl isotopomers of the halogenated species.

Novel Aspects: Graphical visualization of ultrahigh resolving power ESI/FT-ICR MS along with proton affinity differences and other multistage MS can be used for highly confident detection/characterization of pesticides in complex sample mixtures.

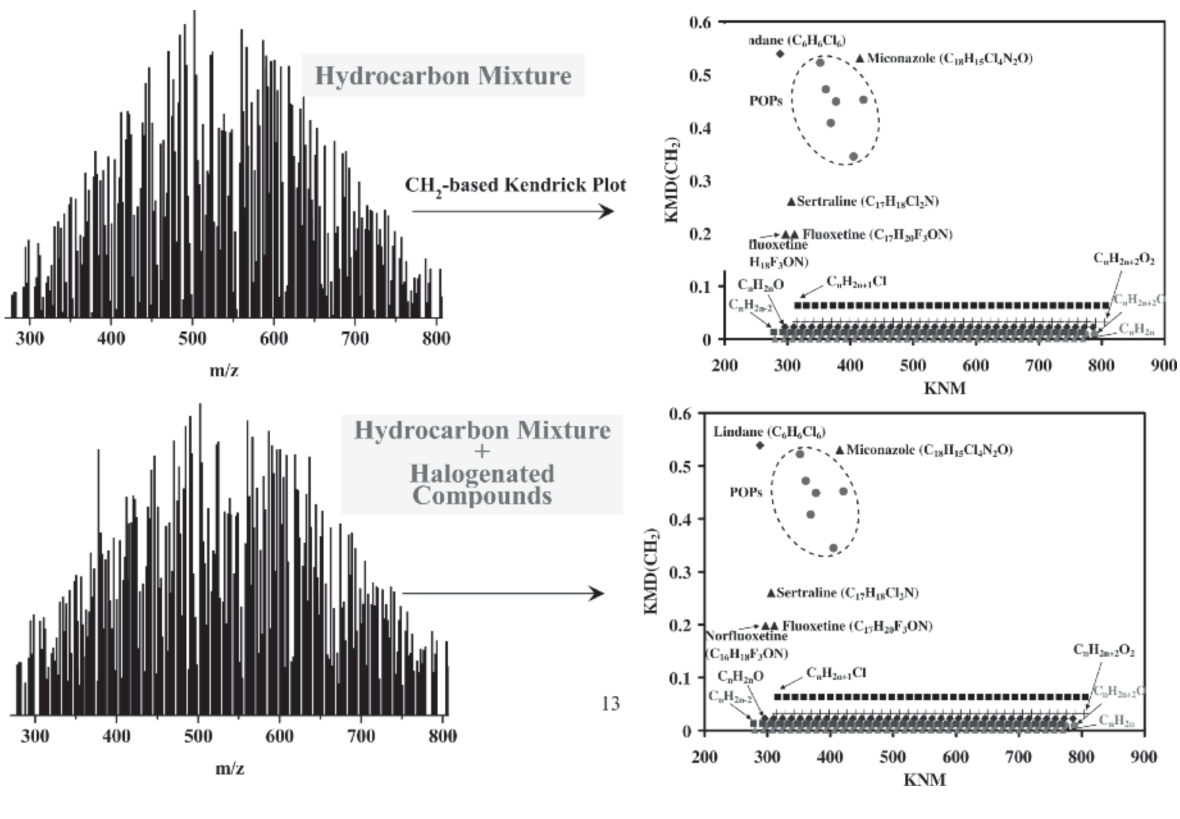


Figure 3. Kendrick Plots: "Rapid" Pollutant Identification in Complex Mixtures

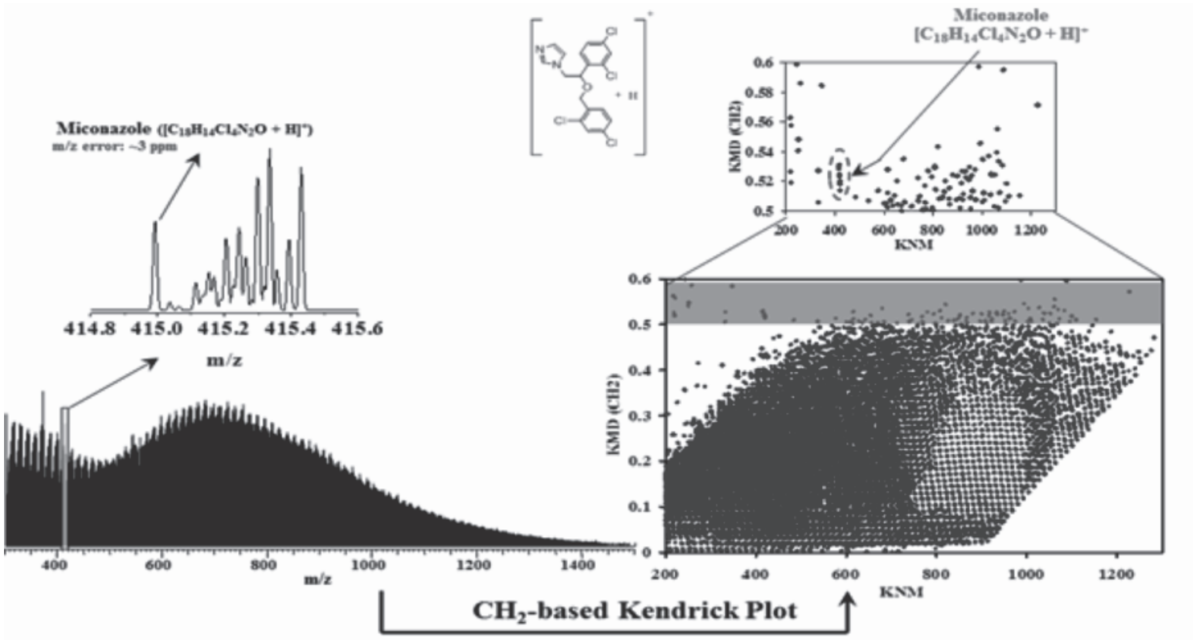


Figure 4. Asphalt-Toluene Extract (Spiked at ~1ppb of Miconazole)

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THE IMPACT OF KURA RIVER FLOODS ON SPREADING OF OBSOLETE PESTICIDES IN THE ENVIRONMENT OF AZERBAIJAN

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The length of Kur-river is 1515 km, 980 km of which run through the territory of Azerbaijan. Its the biggest river in Azerbaijan providing 70% of water supply of the country. In April 2010 the water level in Kura started rising hourly and flow speed increased from 500 m^3 sec^{-1} to 2,500 m^3 sec^{-1}, what created an emergency situation in the provinces of Azerbaijan. According to official statistics report, 110 thous. hectares of land went under the water, of which 60 thous. hectares comprised fertile arable lands. These lands had long been used for agricultural developments during the former Soviet Union. According to Statistics Committee of Azerbaijan, in 1990, the total usage of pesticides in the agricultural areas comprised 87 kg per hectare. In 1985, the usage rate was 166 kg per hectare.

The recent flood washed away large obsolete pesticide stocks in the former chemical warehouses adjacent to agricultural areas in Salyan, Neftchala, Sabirabad, Saatli and other regions. Five villages in Sabirabad region completely stayed under the water for a lengthy period, the reason why people flee these villages. The official statistics in Azerbaijan indicate that 3,741 thous. hectares of arable lands underwent serious degradation due to the flooding. This makes 41% of the total arable land area.

Along Kur-river, in Aghstafa-Qazakh and central lowland regions of Azerbaijan there are ~38-40 thous. tonnes of obsolete pesticides either buried or stored in old warehouses. Flood washed away and disseminated to vaster areas the remainders of these obsolete pesticides in Sabirabad, Neftchala, Salyan, Imishli and other regions located in Kur-river lowland. This eventually resulted in the decrease of the biosenosys of these areas by 60-70%. According to the estimated reports between 1995-2010, the area of degraded land increased by ~20 thous. hectares.

Kur-river also destroyed storages of mineral fertilizers, that caused salinization of these areas.

Every time, flood covers area of about 500 meters at both sides of Kur river. That makes ~2,000 hectares of fertile land. In Salyan and Neftchala regions, where the largest obsolete pesticide stocks exist, the lands along Kur-river are of no use any more and require high investment for restoration. Population living in these area, especially children, exposed to high human health risks.

The 105 thous. hectares of land on both sides of Kur-river used to be covered by riverine tugay forests. In some areas, these forests used to extend to over 10 km along the river. Tuqay forests maintained fertility of lands and served as a barrier to flooding. Later on, the large area of forest had been destroyed to open space for construction of dam, and this resulted in decrease of tugay forest area along Kur-river.

During floods, the water covers whole villages for a lengthy period and this impacts not only the infrastructure. It stays in the pits, destroying arable lands and forests, causing serious damage to natural ecosystems. Thus, heavily pesticide polluted water stayed for almost four months around Sarisu lake –Sabirabad, Askerbayli, close to Qasimbayli village. Then it was pumped back to Kur without any treatment, regardless Kur-river river being a source of drinking water for tens of thousands of people.

The situation in Sabirabad is very similar to other areas, where flood water stays for up to four months, creating bogs and causing damage to fertility of soil in the affected areas.

Recommended actions to be taken in the near future are as follows:

1. Raise public awareness, particularly in the areas regularly affected by floods.
2. Quantify the volume of obsolete pesticides and fertlisers near-by Kur-river and prioritise them for clean-up and disposal (this step is in the process by the Government)
3. Improve pesticide management system
4. Clean oozy river bed and to define works for moving small ships there. Moving of ships is one of the methods for preventing river delta from oozing.
5. Strengthen dams along the Kur-river. Our survey field trips recorded that the width of the dams makes 4-5 meters and this is not strong enough.
6. Restore of Tuqay forests along the Kur-river. In 1950, Tuqay forests occupied area of 105 thous. hectares. Nowadays the area decreased to 50 thousand hectares according to official data.
7. Initiate som cleaning and restoration works in the areas covered by floods, bog and prioritize small lakelets.

SESSION 4. APPROACHES FOR SUSTAINABLE PESTICIDE MANAGEMENT

SAVE AND GROW: FAO'S NEW PARADIGM FOR SUSTAINABLE CROP PRODUCTION INTENSIFICATION

Richard Thompson (AGP) and Walter de Oliviera (AGS)
UN Food and Agriculture Organisation

The Green Revolution in agriculture, which swept much of the developing world during the 1960s, saved an estimated one billion people from famine. Thanks to high-yielding crop varieties, irrigation, agrochemicals and modern management techniques, farmers in developing countries increased food production from 800 million tonnes to more than 2.2 billion tonnes between 1961 and 2000. Intensive crop production helped to reduce the number of undernourished, drive rural development and prevent the destruction of natural ecosystems to make way for extensive farming. Those achievements came at a cost. In many countries, decades of intensive cropping have degraded fertile land and depleted groundwater, provoked pest upsurges, eroded biodiversity, and polluted air, soil and water. As the world population rises to a projected 9.2 billion in 2050, we have no option but to further intensify crop production. But the yield growth rate of major cereals is declining, and farmers face a series of unprecedented, intersecting challenges: increasing competition for land and water, rising fuel and fertilizer prices, and the impact of climate change.

The present paradigm of intensive crop production cannot meet the challenges of the new millennium. In order to grow, agriculture must learn to *save*. Consider, for example, the hidden cost of repeated ploughing. By disrupting soil structure, intensive tillage leads to loss of nutrients, moisture and productivity. More farmers could save natural resources, time and money if they adopted conservation agriculture (CA), which minimizes tillage, protects the soil surface, and alternates cereals with soil-enriching legumes. Those simple practices help to reduce crops' water needs by 30 percent and the energy costs of production by up to 60 percent. In trials in southern Africa, they increased maize yields six-fold. Combining CA with precision irrigation produces more crops from fewer drops. Farmers can reduce the need for fertilizers by adopting "precision placement", which doubles the amount of nutrients absorbed by plants. By using insecticides wisely, they can save pest predators and disrupt the cycle of pest resistance. Economizing on agrochemicals and building healthy agro-ecosystems would enable low-income farm families in developing countries – some 2.5 billion people – to maximize yields and invest the savings in their health and education.

This new paradigm of agriculture is sustainable crop production intensification (SCPI), which can be summed up in the words "save and grow". Sustainable intensification means a productive agriculture that conserves and enhances natural resources. It uses an ecosystem approach that draws on nature's contribution to crop growth – soil organic matter, water flow regulation, pollination and natural predation of pests – and applies appropriate external inputs at the right time, in the right amount. "Save and grow" farming systems offer proven productivity, economic and environmental benefits. A review of agricultural development in 57 low-income countries found that ecosystem farming led to average yield increases of almost 80 percent. Conservation agriculture, which is practised on more than 100 million hectares worldwide, contributes to climate change mitigation by sequestering in soil millions of tonnes of carbon a year.

SCPI represents a major shift from the homogeneous model of crop production to knowledge-intensive, often location-specific, farming systems. Its application will require significant support to farmers in testing new practices and adapting technologies. Governments will need to strengthen national programmes for plant genetic resources conservation, plant breeding and seed distribution in order to deploy improved crop varieties that are resilient to climate change and use nutrients, water and external inputs more efficiently. Fundamental changes are also required in agricultural development strategies. Policymakers must provide incentives for adoption of SCPI, such as rewarding good management of agro-ecosystems. Developed countries should support sustainable intensification by increasing considerably the flow of external assistance to, and investment in, agriculture in the developing world.

Sustainable intensification of smallholder crop production is one of FAO's strategic objectives. Our aim over the next 15 years is to assist developing countries in adopting "save and grow" policies and approaches. FAO has published the book "Save and Grow" as a toolkit of adaptable farming systems, technologies and practices, and explores the policies and the institutional arrangements that will support the large-scale implementation of SCPI.

The "Save and Grow" book together with the accompanying fact sheets is available to be read on-line in Arabic, Chinese, English, French, Russian and Spanish at http://www.fao.org/ag/save-and-grow

An overview of the main chapters of Save and Grow is included as Annex A.

1. The challenge

To feed a growing world population, we have no option but to intensify crop production. But farmers face unprecedented constraints. In order to grow, agriculture must learn to save.

The Green Revolution led to a quantum leap in food production and bolstered world food security. In many countries, however, intensive crop production has depleted agriculture's natural resource base, jeopardizing future productivity. In order to meet projected demand over the next 40 years, farmers in the developing world must double food production, a challenge made even more daunting by the combined effects of climate change and growing competition for land, water and energy. This book presents a new paradigm: sustainable crop production intensification (SCPI), which produces more from the same area of land while conserving resources, reducing negative impacts on the environment and enhancing natural capital and the flow of ecosystem services.

2. Farming systems

Crop production intensification will be built on farming systems that offer a range of productivity, socio-economic and environmental benefits to producers and to society at large.

The ecosystem approach to crop production regenerates and sustains the health of farmland. Farming systems for SCPI will be based on conservation agriculture practices, the use of good seed of high-yielding adapted varieties, integrated pest management, plant nutrition based on healthy soils, efficient water management, and the integration of crops, pastures, trees and livestock. The very nature of sustainable production systems is dynamic: they should offer farmers many possible combinations of practices to choose from and adapt, according to their local production conditions and constraints. Such systems are knowledge-intensive. Policies for SCPI should build capacity through extension approaches such as farmer field schools, and facilitate local production of specialized farm tools.

3. Soil health

Agriculture must, literally, return to its roots by rediscovering the importance of healthy soil, drawing on natural sources of plant nutrition, and using mineral fertilizer wisely.

Soils rich in biota and organic matter are the foundation of increased crop productivity. The best yields are achieved when nutrients come from a mix of mineral fertilizers and natural sources, such as manure and nitrogen-fixing crops and trees. Judicious use of mineral fertilizers saves money and ensures that nutrients reach the plant and do not pollute air, soil and waterways. Policies to promote soil health should encourage conservation agriculture and mixed crop-livestock and agroforestry systems that enhance soil fertility. They should remove incentives that encourage mechanical tillage and the wasteful use of fertilizers, and transfer to farmers precision approaches such as urea deep placement and site-specific nutrient management.

4. Crops and varieties

Farmers will need a genetically diverse portfolio of improved crop varieties that are suited to a range of agro-ecosystems and farming practices, and resilient to climate change.

Genetically improved cereal varieties accounted for some 50 percent of the increase in yields over the past few decades. Plant breeders must achieve similar results in the future. However, timely delivery to farmers of high-yielding varieties requires big improvements in the system that connects plant germplasm collections, plant breeding and seed delivery. Over the past century, about 75 percent of plant genetic resources (PGR) has been lost and a third of today's diversity could disappear by 2050. Increased support to PGR collection, conservation and utilization is crucial. Funding is also needed to revitalize public plant breeding programmes. Policies should help to link formal and farmer-saved seed systems, and foster the emergence of local seed enterprises.

5. Water management

Sustainable intensification requires smarter, precision technologies for irrigation and farming practices that use ecosystem approaches to conserve water.

Cities and industries are competing intensely with agriculture for the use of water. Despite its high productivity, irrigation is under growing pressure to reduce its environmental impact, including soil salinization and nitrate contamination of aquifers. Knowledge-based precision irrigation that provides reliable and flexible water application, along with deficit irrigation and wastewater-reuse, will be a major platform for sustainable intensification. Policies will need to eliminate perverse subsidies that encourage farmers to waste water. In rainfed areas, climate change threatens millions of small farms. Increasing rainfed productivity will depend on the use of improved, drought-tolerant varieties and management practices that save water.

6. Plant protection

Pesticides kill pests, but also pests' natural enemies, and their overuse can harm farmers, consumers and the environment. The first line of defence is a healthy agro-ecosystem.

In well managed farming systems, crop losses to insects can often be kept to an acceptable minimum by deploying resistant varieties, conserving predators and managing crop nutrient levels to reduce insect reproduction. Recommended measures against diseases include use of clean planting material, crop rotations to suppress pathogens, and eliminating infected host plants. Effective weed management entails timely manual weeding, minimized tillage and the use of surface residues. When necessary, lower risk synthetic pesticides should be used for targeted control, in the right quantity and at the right time. Integrated pest management can be promoted through farmer field schools, local production of biocontrol agents, strict pesticide regulations, and removal of pesticide subsidies.

7. Policies and institutions

To encourage smallholders to adopt sustainable crop production intensification, fundamental changes are needed in agricultural development policies and institutions.

First, farming needs to be profitable: smallholders must be able to afford inputs and be sure of earning a reasonable price for their crops. Some countries protect income by fixing minimum prices for commodities; others are exploring "smart subsidies" on inputs, targeted to low-income producers. Policymakers also need to devise incentives for small-scale farmers to use natural resources wisely – for example, through payments for environmental services and land tenure that entitles them to benefit from increases in the value of natural capital – and reduce the transaction costs of access to credit, which is urgently needed for investment. In many countries, regulations are needed to protect farmers from unscrupulous dealers selling bogus seed and other inputs. Major investment will be needed to rebuild research and technology transfer capacity in developing countries in order to provide farmers with appropriate technologies and to enhance their skills through farmer field schools.

DEMONSTRATION AND SCALING UP SUSTAINABLE ALTERNATIVES TO DDT FOR CONTROL VECTOR BORN DISEASES IN SOUTHERN CAUCASUS AND CENTRAL ASIA

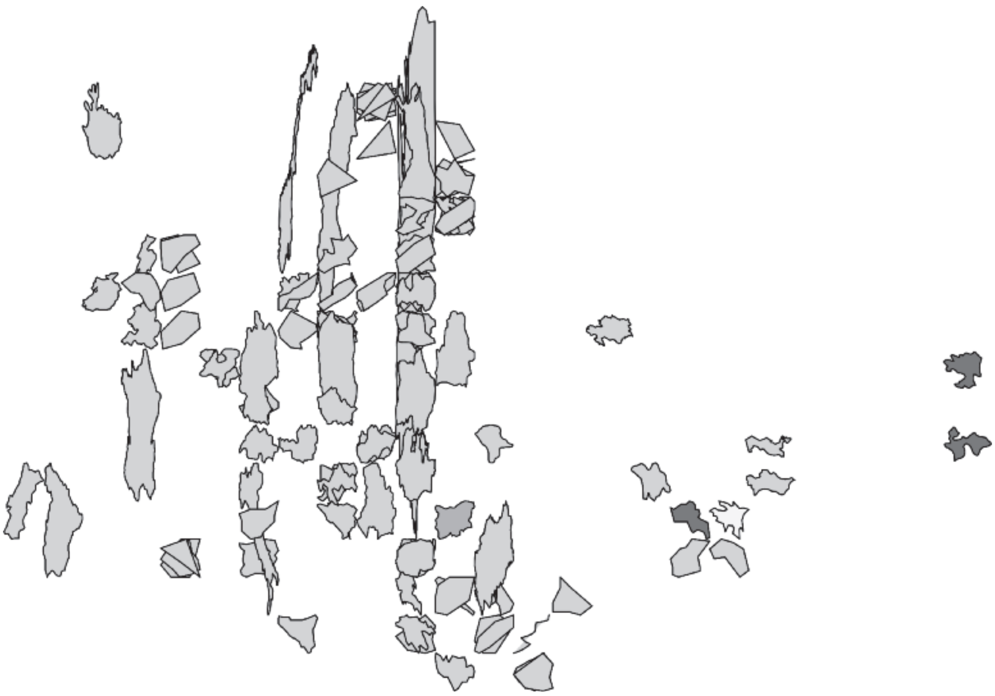
Khatuna Akhalaia
Milieukontakt International, Georgia

The project goals are to reduce reliance on persistent insecticides, including DDT, without increasing the occurrence and spread of malaria and other VBDs; to promote appropriate vector control management practices by strengthening capacities and capabilities of countries to implement environmentally sound, effective and sustainable vector control alternatives; and to reduce the availability of DDT stocks to the population through safeguarding of relevant stocks. The Project is focused on Georgia, Kyrgyzstan and Tajikistan.

The project is divided into two parts. Health part – WHO (1-2) which is implementing by WHO representatives in countries and second the environmental part implementing by Milieukontakt International (3).

Project duration is 5 years. - GEF/UNEP - 2010-2015.

In the frame of the Project, Milieukontakt Amsterdam has been contracted by Green Cross Switzerland to undertake the following actions:



- undertake an integrated management approach for the participatory safeguarding of (on average) 60 tonnes of prioritised POPs stockpiles per country and the development of participatory disposal concepts (mainly DDT) as example for similar projects in other countries in the region;
- present measures to safeguard stockpiles; and
- communicate on the hazards of DDT to specific target groups.

Steps implemented b 2010-2011 in Tajikistan, Kyrgyzstan and Georgia

Tajikistan and Kyrgyzstan:

Training inventory was already done in the frame of FAO/Turkey project, and inventory groups were established for both countries. In spring 2012, both countries will start inventory activities according to the FAO standard, and all data will be available in PSMS database after completing the inventory for the whole country.

DDT project will proceed with the repackaging of 60t of DDT or DDT containing obsolete pesticides and associated wastes. Final disposal of repacked pesticides will be implemented with planed project FAO- EC.

Most important part is that in both countries it is possible to make one complete model from Inventory till destruction with local working group.

Georgia

In the frame of EECCA FAO project, there will be 18 inventory sites. Repackaging of DDT or associated waste will be completed in the frame of the DDT UNEP/WHO project. The final destruction of UNDP GEF project is ongoing.

MKI - Planning for 2012

	Jan	Feb	March	April	May	June
Georgia			Platform meeting of stakeholders	Inventory		PSMS
Kyrgyzstan			Platform meeting of stakeholders	PSMS		
Tajikistan			Platform meeting of stakeholders	PSMS		
Azerbaijan			Start og the project			
	July	Auv.	September	October	Nov.	Dec.
Georgia			Platform meeting of stakeholders	repackaging		
Kyrgyzstan		Platform meeting of stakeholders	repackaging			

Tajikistan		Platform meeting of stakeholders	Repackaging			
Azebaijan			Inventory	PSMS		

In the future, it is planned to include Azerbaijan in the future activities as new project will be initiated in December 2011.

Potential outcomes of the project are as follows:

Outcome 1: Demonstrated viability and cost-effectiveness of alternatives vector control interventions to persistent insecticides that are appropriate to the major eco-epidemiological, environmental and socio-cultural settings

- To design research protocols for each participating country with assistance provided by an international expert and WHO: international expert recruited and expert advice rendered (February-March 2011): COMPLETED
- To implement and monitor project activities including support for procurement of items in demonstration sites: international expert and NPC/project staff recruited and expert advice being rendered, country-level trainings completed, project progress being reported and relevant procurements done (April 2011-October 2014): ONGOING
- To evaluate project activities: expert advice being provided, project data being processed and analyzed, and progress reports being prepared (October 2011-November 2014): ONGOING

Outcome 2: Enhanced national capacity for planning and implementation of IVM

To formulate and draft regional IVM policy and strategy: international expert recruited, a first draft developed and being discussed: *ONGOING*

- To design regional technical guidelines and training/learning materials on IVM: international expert recruited and their content discussed and agreed: *ONGOING*

Outcome 4: Existing regionally coordinated mechanisms for effective dissemination and sharing of specific project/country experiences supported

- To develop and agree on specific communication activity plans for health sector: local/international experts recruited, expert advice rendered and communication activity plans for health sector developed *(2012-2015): NOT INITIATED YET*

MAIN ACTIVITIES FOR HEALTH SECTOR, 2012

- To finalize regional IVM policy and strategy and communication activity plan for health sector: *International expert will be recruited in close collaboration with WHO/Europe in February 2012*
- To design and finalize regional technical guidelines and training/learning materials on IVM: *International expert will be recruited in close collaboration with WHO/Europe in April-May 2012*
- To conduct a regional consensus workshop on regional IVM policy and strategy and on development of national IVM policy framework: *A regional workshop will be conducted in September-October 2012*
- To implement and monitor project

activities in demonstration sites: *Expert advice rendered and progress with project implementation being monitored and reported (January – December 2012)*

- To evaluate project activities: *Expert advice rendered, project data processed and analyzed, and progress reports being prepared (January - December 2012)*

OBSOLETE PESTICIDES TECHNICAL STUDY IN KYRGYZ REPUBLIC (WORLD BANK PROJECT 100020592)

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A number of sites, where obsolete pesticides are either kept in storage or buried were investigated for this technical study. This project was implemented in the following five stages: training, inventory, characterization and prioritization of obsolete pesticide containing sites, risk assessment in priority burial sites, identification and feasibility assessment of safeguarding, transport and elimination/disposal options of identified stocks and other contaminated wastes, feasibility of in situ site remediation/containment alternatives for highly contaminated burial sites.

The national working group (NWG) of the project noted the professional work of experts of Tauw Consortium and expressed deep gratitude for a professional research work. By The "An Integrated Recovery" is the optimal solution to the problems of obsolete pesticides (OP), in comparison with known experience on solving problems in the CIS countries (Ukraine, Moldova). Therefore, this "Option of Integrated Recovery" was preferred by the State Agency on Environment Protection and Forestry under the Government of the Kyrgyz Republic for future project in Jalal-Abad district.

NWG expressed the following views, which should be taken into the account when developing the future project:

1. To exclude activities on transportation 500 m³ / 250 tonnes of OP to former Jalal-Abad Agrochemical Store and to the Central Store (CS) in local administration Sarai village (Osh) due to number of significant reasons:
   - Jalal-Abad Store is private, and definitely the owner will not agree with storage of repacked OP from the whole oblast, even it is temporarily.
   - It will also save significant funds – it will be not necessary to repair the facilities of former Agrochemical Store in Jalal-Abad town.
   - For obtaining agreement for transportation and storage of additional volumes of OP in SC in local administration of Sarai village, it is necessary to obtain such agreement from local authorities. But it is clear, that they would not agree with this. The participants of the meeting insisted on the including 90 tonnes of OP from Central Store of local administration of Sarai village (Osh) to the vitrification process.
2. All collected and repacked OP from Jalal-Abad district and Central Store in local administration of Sarai village should be transported immediately to the site Suzak A. At the same time it is necessary to build light sheds with light construction for temporary (1 year) storage of repacked OP up to their disposal by method of vitrification.
3. For bioremediation, it should be allowed to use the methods of selection of strains along with technology of oxidation and reduction.
4. To carry out tests for selection of local plants for phytoremediation.
5. To include to the plan of project activities creating information system (web-site) for collection information on work being done on OP in KG.

TC - Tauw Consortium

NWG - national working group

OP – Obsolete pesticides

Storage sites at Jalal Abad district

The Jalal Abad district encompasses numerous badly maintained former pesticide storage sites with obsolete pesticides, waste and persistent organic pollutant pesticides (referred to as OPs). 25 of these storage sites were indentified and visited by TC and trainees to make an inventory and risk assessment in relation to the OPs and their environmental threat. Buried OPs and heavily contaminated topsoil are problems at many of these sites, most of which are private property. Risk assessments reveal that ten of the 25 sites are high-priority sites. In total, these sites have 250 tonnes of OPs and 145 m^3 of heavily contaminated soil. Measures to eliminate acute risks in the short term are required at these sites, including measures such as repackaging, removal and safe storage of OPs, soil remediation and, finally, destruction of the OPs. Before a cleanup campaign can be executed, the quantities of OPs, buried pesticides and heavily contaminated topsoil need to be updated because the situation at privately owned sites can change overnight.

In addition to the ten high-priority storage sites, there are nine low-priority sites that do not have OPs but probably do have contaminated topsoil. At least two have buried pesticides. The TC proposes to further assess the topsoil and the pits to determine the quantity of contaminated soil and the quantity of buried pesticides at these sites. If these surveys reveal that the sites have buried OPs and contaminated soil and that there are environmental risks, the cleanup of these sites can be incorporated into the Jalal Abad oblast cleanup campaign.

Burial site Suzak A

The original design of the Suzak A burial site is good, but pesticides at the site are now exposed and have been spread through the area by 'illegal waste miners'. DDT, in particular, is removed from the site to be sold on local markets. The total estimated exposed pesticide quantity is approximately 1,000 tonnes; the amount still buried in the trenches is estimated at approximately 2,000 tonnes (October 2009). OPs have contaminated the topsoil and the rainwater collected in pits and potholes is contaminated. Over the years, pesticides have seeped into approximately 15,000 m^2 of soil. The estimated volume of heavily contaminated soil is 8,250 m^3, the volume of contaminated soil is 5,000 m^3 and the volume of slightly contaminated soil is 4,500 m^3.

The situation at the burial site poses a direct and unacceptable threat to public health and the environment and urgent measures must be taken. 35 cattle and 12 sheep died after drinking standing rainwater contaminated with OPs at the Suzak A burial site in March 2010. The owners of the lifestock quickly sold the contaminated meat, resulting in the hospitalization of 20 consumers. This sad incident underlines the seriousness and urgency of this issue and the need to address it as soon as possible.

Selection of most appropriate rehabilitation alternative

In order to come up with a group of well balanced measures to mitigate or eliminate the risks at the burial site and storage sites, TC assessed the relative merits of four rehabilitation alternatives in terms of risk reduction, environmental benefits and costs. In the short term, the TC proposes elimination of the acute risks at the storage sites and the Suzak A burial site in an integrated approach (Phase 1). For the medium-term, the TC proposes elimination of the remaining risks related to the contained OPs at the Suzak A burial site based on destruction of these OPs (Phase 2). For the long term, the TC proposes addressing the risk related to the contaminated soil at the Suzak A burial site (Phase 3).

Phase 1 - short-term measures to be taken to eliminate the acute risks

The following short-term actions are proposed to reduce the acute risks of the storage sites and the Suzak A burial site:

- At the 10 high-priority storage sites, execute surveys to update the amounts of buried obsolete pesticides and contaminated soil. Repack the 250 tonnes of OPs and excavate the 145 m^3 of heavily contaminated topsoil. Transport the contaminated soil to the Suzak A burial site for containment, along with the pesticides and contaminated soil already present at this site
- Appoint capable managers to the Suzak A burial site. Fence the site and hire guards to keep trespassers and lifestock off the site and further reduce risk. Repair and update the old surface drainage system and implement erosion control measures
- Collect 1,000 tonnes of OPs exposed to the

open air at the Suzak A burial site and place these them in trenches. Then cap the trenches with available soil. Contain these 1,000 tonnes with the 2,000 tonnes of OPs that are stilled buried at the site until on-site destruction is arranged

- Carry out an on-site and/or in-situ OPs destruction pilot. The available project budget (EUR 3 million) should cover the in-situ destruction by vitrification of 1,700 tonnes of OPs and 3,400 tonnes of heavily contaminated soil

On-site and/or in-situ treatment techniques (e.g. vitrification, thermal desorption, and Supercritical Water Oxidation (SCWO) with Base Catalyzed Decomposition (BCD)) seem to be the most suitable and robust techniques. Vitrification is a particularly interesting technique because it combines soil remediation and destruction of OPs. To vitrify one-third of OPs, two-thirds of (contaminated) soil is needed as a matrix.

Phase 2 - medium-term measures

Based on the experience done up in in-situ pilot and on-site destruction efforts, the remaining 1,550 tons of OPs and 3,100 tons of heavily contaminated soil can be destroyed with the same technique once the Kyrgyz authorities have gathered sufficient funding. If the Kyrgyz authority is able to gather sufficient funding to cover the costs of in-situ and/or on-site destruction, the costs of the final, sustainable solution are limited to management, containment and destruction costs. With in-situ and/or on-site destruction, there are no extra costs for repackaging and (international) transport off-site. The money saved can be spent on in-situ and/or on-site destruction. Once the technique is operational, it should be considered for use in the destruction of OPs from other burial sites, such as the Suzak B and Naryn burial sites, as well as for the destruction of the 200 tons of OPs stored in the Intermediate Collection Centre in Osh.

Phase 3 - long-term measures

In this phase, all of the risks related to the presence of contaminated topsoil at the burial site are addressed. To avoid expensive transport costs for large quantities of soil, on-site treatment of all contaminated soil is recommended. The remaining (heavily) contaminated soil can be remediated with the oxidation, reduction technique. Phytoremediation is a viable option for the remediation of slightly contaminated soil. The soil remediation techniques and the volumes of soil to be treated are:

- Oxidation and reduction techniques
  - 4,800 m^3 (8,400 m^3 minus 3,600 m^3) of heavily contaminated soil
  - 4,000 m^3 contaminated soil
- Phytoremediation
  - 3,500 m^3 slightly contaminated soil

UNWISE ALTERNATIVE EFFORTS TO CONTROL MOSQUITO MAY BE CAUSES OF SEVERAL DISEASES

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Abstract

Malaria is still a threat in Bangladesh as in many countries although a concerted effort was initiated for the eradication of its mosquito vector by applying DDT during the 60's. At one point, eradication of malaria was acclaimed but later on it reappeared along with other virulent fevers like Kaalazar and Dengue. Use of DDT is no more legally allowed in Bangladesh, which has been officially replaced by a number organophosphates and/or synthetic pyrethroids and their combinations in addition to the Integrated Vector Management (IVM) package. IVM being a labour-intensive community approach is still to go a long way to be mass popular. Adulticides, larvicides, residual sprays, mosquito coil, insecticide-impregnated curtain, aerosol etc. still serve as the major weapons of mosquito control. Thus mosquito control still mostly depends on chemical insecticides. Although use of DDT is banned in Bangladesh, there are reports on their illegal use in different forms. Moreover, there is tons of left-over DDT in Bangladesh, which is likely to cause several diseases. As per one report, about 500 MTs of DDT stockpiles are lying in the Medical Sub-Depot at Chittagong for over a period of 26 years. DDT is a persistent organic pollutant (POP) pesticide, which can cause diseases like cancer, endocrine disorder, disruption of immune system, embryonic abnormality, reproductive disorder, etc. Other chemical insecticides, which are replacing DDT, are also not free from hazardous impacts. IVM thus appears to be a wise approach requiring concerted efforts for the management of mosquito to control malaria. Such an IVM comprises use of *Bacillus thuringiensis* Berliner var. *israelensis* (B.t.i.), methoprene, biocontrol agents, cleaning of breeding sites, pyrethroid-impregnated curtain etc. Therefore, a wise effort should be to completely stop the use of DDT, elimination of its stockpiles wherever they are in Bangladesh and to popularize the IVM throughout the country.

Key words: Persistent Organic Pollutant, DDT, Mosquito coil, aerosol, Integrated Vector Management

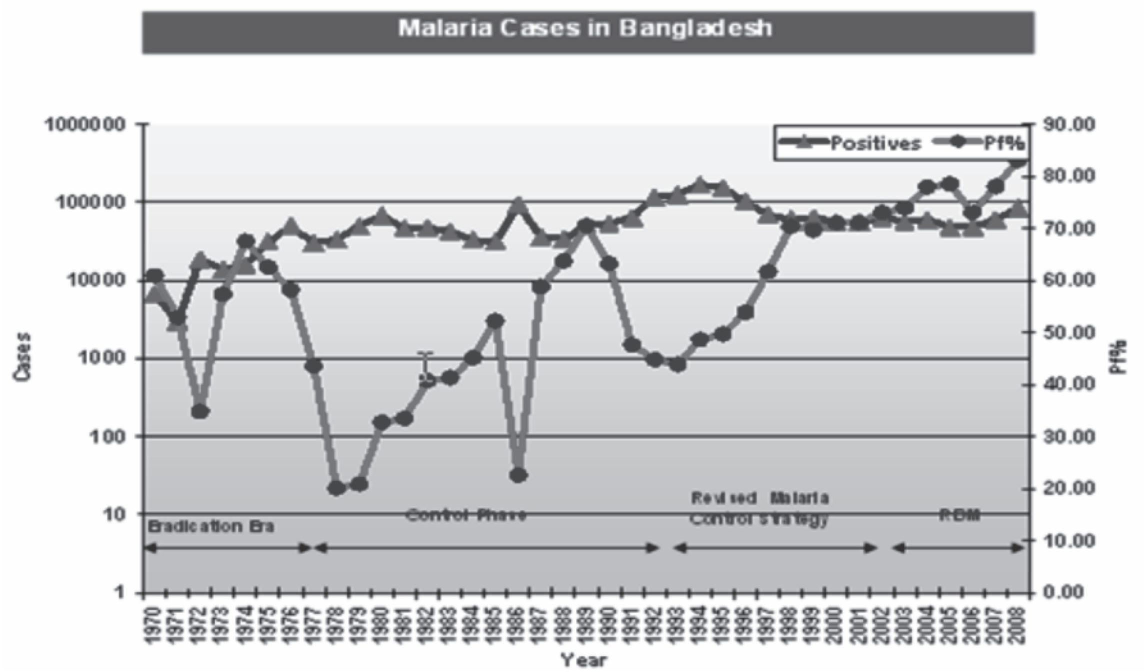
Introduction

Malaria caused by 4 organisms such as *Plasmodium vivax, P. ovale, P. malariae* and *P. falciparum* still is a serious threat in many parts of Bangladesh. These are transmitted by 7 species of mosquitoes of which 4 are most important. These are: *Anopheles dirus,* a wild species found both in out-door and in-door occurs in hilly forested and foot hill areas, *A. minimus* occurs in hilly forested and foot hill areas – a primary vector, which was eliminatedthrough Malaria Eradication Program (MEP) using DDT, is recently reappearing, *A. philippinensis*occurs inflood plain deltaic region was also eliminated through MEP is scarcely found now, and *A. sundaicus*occurs in coastal areas was virtually eliminated through MEP but is recently reappearing. Other than these, *A. annularis* usually found in large numbers, is an important vector in some places, *A. aconitus* not common is secondary vector in some places and *A. vagus* fairly common all over Bangladesh has been recently incriminated as vector. Besides, 79 Culicine species are recorded of which *Culex quinquefasciatus*is a vector of Filariasis disease, and *Aedes aegypti* and *Ae. albopictus*are suspected as vectors of dengue. DDT because of its health hazardous effects has been banned in 1998 in Bangladesh in compliance with the Stockholm Convention and a number of chemicals in different forms are now used as substitutes of DDT. Now the question is: Are these chemical substitutes free from any health hazardous effects? To find out answers to this question a review has been made and compiled in this article.

Findings

Malaria Eradication Program (MEP) was

successfully carried-out with residual spray of DDT supplied by WHO during 1960 – 1977 (Eradication Era) resulting in complete eradication of malaria/mosquito in 1977. But the malaria again started reappearing. The use of DDT was continued for mosquito control during 1971-1992 (Control Phase) with DDT produced inside the country along with donor-supplied DDT. Subsequently Revised Malaria Control Strategy (1993-2002) was adopted that included restricted use of DDT and other control measures including insecticide treated nets (ITNs) and Long Lasting Insecticidal Nets (LLIN). The DDT was subsequently banned in 1998 following which the use of DDT was highly restricted. The resurgence of malaria continued (Roll Back Malaria) and still malaria is observed in many parts of Bangladesh. DDT is no more produced in the country and is also not imported.



Pf: Plasmodium falciparum
SPR: Slide Positivity Rate (Positive case per 100 slides examined)
SFR: Slide falciparum rate (Pf infection per 100 slides examined)

No epidemic was reported in 2008.However, Chittagong, Netrakona and Cox's Bazar were affected by malaria epidemics in 2004 whereas Netrakona alone was affected by the epidemics in 2005.

The discontinuation of DDT as well as import of substandard DDT caused obsolete DDT stockpiles in different locations of Bangladesh. A total of 602.389 MTs comprising 482.904 MTs of substandard DDTin 4 Medical Sub-Depots in Chittagong out of 500 MTs imported by the Health Directorate through ADB finance in 1984, 101.69 MTs of DDT technical at Bangladesh Chemical Industries Corporation (BCIC), Chittagong, 12.795 MTs of DDT 75 WP at district godowns of Directorate of Health (DOH) and 0.005 MTs of DDT 75 WP at district godowns of Department of Agricultural Extension (DAE) have been stockpiled in Bangladesh. The very poor storage conditions are resulting in seepage, pilferage, weathering and misuse of DDT, which are contaminating the environment and are suspected to cause serious health hazards such as cancers and tumors (Particularly breast cancer in women), neurobehavioural impairment including learning disorders, endocrine system disruption, reproductive deficits and sex-linked disorders (Birth-defects/premature birth of baby), and a shortened period of lactation in nursing mothers and increased rate of diabetes to the surrounding affected human residents.

Currently peoples are using different alternatives for getting rid of mosquito biting, nuisance, high pitched buzzing, dengue fever, filariasis and malaria. These alternatives include mosquito coils, mats, aerosols and vaporizers prepared with synthetic pyrethroids (SP) and organophosphate (OP) insecticides (Table 1) along with other adjuvants and fillers. Review ofpublished articles reveals that most of these products have adverse effects, which may cause several diseases in the affected human beings.

Probable Health Risks of Mosquito Coils/Mats

SPs are major a.i. accounting for about 0.3-0.4% of coil mass, the lowest lethal oral dose of which is 750 mg/kg for children and 1,000 mg/kg for adults. Pyrethrins are of low chronic toxicity to humans and low reproductive toxicity in animals, although headache, nausea, and dizziness are observed in male sprayers. But the remaining components of mosquito coil are organic fillers, binders, dyes, and other additives. Their combustion generates large amounts of submicrometer particles [(particulate matter < 2.5 [micro]m in diameter; P[M.sub.2.5])] and gaseous pollutants. Burning one mosquito coil generates P[M.sub.2.5] = burning 75-137 cigarettes. Coil smoke contains a suite of volatile organic compounds (VOCs), including human carcinogens and suspected carcinogens. Submicrometer particles can reach lower respiratory tract and may be coated with a wide range of organic compounds, some of which are carcinogens or suspected carcinogens [(polycyclic aromatic hydrocarbons (PAHs)]. Gas phase of coil smoke contains some carbonyl compounds (e.g. formaldehyde and acetaldehyde- as much as 55%) with properties that can produce strong irritating effects on upper respiratory tract. The emission of formaldehyde from burning one coil is equal to burning 51 cigarettes. Long-term exposure to coil smoke inducesasthma and persistent wheeze in children. Benz[a]anthracene, benzo[a]pyrene, benzo[b] fluoranthene, benzo[k]fluoranthene, dibenz[a,h] anthracene, and indeno[1,2,3-ca] pyrene are classified by the U.S. EPA as probable human carcinogens. Acrolein,glyoxal and methyl-glyoxal known for their high reactivity, strong irritation effects and suspected carcinogenic effects are emitted from coil burning. Several VOCs including benzene, toluene, ethylbenzene, p,m,o-xylene, and styrene, are identified in coil smoke. All are known to cause adverse health effects. When mosquito coils containing S-2 (Octachlorodipropyl Ether) are burned, they release a potent lung carcinogen called bischloromethyl ether (BCME).

Probable Health Risks of Aerosol

An aerosol spray often consists of very small droplets of solvent, propellant and AI. Major AIs are SP, which are relatively safer. But most industrial aerosols contain organic solvents, which give off vapours that are dangerous if breathed for too long or in too high concentrations. Excessive intake can cause headache, giddiness, mental confusion, blurred vision, nausea, weakness and fatigue, numbness of limbs and, in extreme cases, loss of consciousness. Solvents in contact with skin cause irritation and defatting of the skin. Long-term effects of solvent exposure include damage to the heart, liver, kidneys and central nervous system. Most common propellant, butane, is of relatively low toxicity, but is extremely flammable. But others are potentially hazardous in addition to flammability. Some of very small droplets of solvent, propellant and AI are ideally suited for breathing deep into lungs. Larger droplets are trapped in the nose, throat and upper part of the lung.

Probable Health Risks of Vaporizer

AIs of most vaporizers are SP, which are relatively safer. However, human biomonitoring data revealed urine concentrations of the metabolite (E)-trans-chrysanthemum dicarboxylic acid ((E)-trans-CDCA) between 1.7 microg/l and 7.1 microg/l after 5 minutes of exposure to the different sprays. Also the use of electro-vaporizers led to (E)-trans-CDCA concentrations in the urine in the range of 1.0 microg/l to 6.2 microg/l (1-3 hours exposure period).

Recommendations for Safeway of Mosquito Management

In the above context, the wise alternative to DDT for mosquito/malaria control may only refer to adoption of the Integrated Vector (Mosquito) Management (IVM). This may include to prevent breeding of mosquito removal/cleaning of all breeding sites e.g., bird baths, rain barrels, old automobile tires, ditches, unused swimming/water pools, tree holes, flower pots, roof gutters to avoid stagnant water/ breeding of mosquitoes; to control larvae, the most logical approach, examining each week the presence of larvae, using one or more of the insecticides such as *Bacillus thuringiensis* Berliner var. *israelensis* (B.t.i.), Methoprene, an insect growth regulator (Altosid or any available formulation) to 2nd, 3rd and 4th instar larvae in water, Petrolium distillate oil, Temephos or to control adults by using Adulticides such as Ultra-low volume application (Malathion/ Chlorpyrifos/ Chlorpyrifos+ permethrin), thermal fogging with Malathion/ Chlorpyrifos/Chlorpyrifos+ permethrin as a space treatment against adult mosquitoes at night or early morning when the air is calm (less than 5 mph) or applying Insecticide Residual Spray (IRS) as barrier treatments to tall grasses, weeds, shrubs, fences, and other harborages surrounding parks, playgrounds, residences to help reduce adult mosquito populations, and to avoid Contact of Adult Mosquitoes by using Long-lasting Insecticide Treated Bednets (LLINs)/Insecticides Treated Bednets (ITNs).

Table 1. Substitutes of DDT, Their Formulations and Hazard Classifications

Sl#	Active Ingredient/Class	Formulation Type/Product types	WHO Class	Health Risks
01	Allethrin (SP)	Mat, Aerosol	III	*
02	d-allethrin (SP)	Mat, Coil	II	**
03	d-allethrin (Pynamine Fort) (SP)	Coil	II	**
04	d-trans-allethrin (SP)	Coil	II	**
05	Alpha Cypermethrin (SP)	WP, EC, SC	II	No evidence
06	Bio-allethrin (SP)	Aerosol	II	*
07	S-Bio-allethrin (SP)	Coil	II	**
08	Chlorpyriphos (OP)	EC	II	No evidence
09	Cypermethrin (SP)	EC	II	No evidence
10	Deltamethrin (SP)	Chalk, EC, SC, WP, Flow, DP	II	No evidence
11	Diazinon (OP)	EC	II	No evidence
12	ETOC (Prallethrin) (SP)	Mat, Coil, Vaporizer	II	**
13	Fenthion (OP)	EC	II	No evidence
14	Fenitrothion (OP)	EC	II	No evidence
15	Imiprothin (SP)	Aerosol	III	*
16	Lambda Cyhalothrin (SP)	WP, EC	II	No evidence
17	Malathion (OP)	EC	III	No evidence
18	Metofluthrin (SP)	Coil		**
19	Permethrin (SP)	Aerosol, Powder, EC, WP, DP	II	No evidence
20	Phenthoate (OP)	Liquid, EC	II	No evidence
21	Pirimiphos Methyl (OP)	EC	III	No evidence
22	Pynamine Fort (SP)	Liquid vaporizer	III	*

23	Prallethrin (SP)	Aerosol, Coil, Mat, Vaporizer	II	**
24	Propoxur (Car)	Aerosol	II	*
25	Sumione (SP)	Coil	II	**
26	Temephos (OP)	EC, G	U	No evidence
27	Tetramethrin (SP)	RS, Aerosol	U	*
28	D-Tetramethrin (SP)	Aerosol	U	*
29	Transfluthrin (SP)	Coil	U	**

** Health hazards are most probable through emissions due to ingredients other than Active Ingredients;

* Health hazards are probable through high concentrations and long exposure due to organic solvents and propellant other than butane;

"No evidence" means literatures searched did not indicate significant health hazards under proper use.

WHO Class II means moderately hazardous (non-carcinogenic, non-teratogenic etc.)

WHO Class III means slightly hazardous

WHO Class U means unclassified.

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AN INTEGRATED PEST MANAGEMENT IN THE REPUBLIC OF UZBEKISTAN

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Abstract

The year-round cultivation of many crops is provided by the weather and climatic conditions of Uzbekistan with its characteristic high temperatures. But, as in any southern region, these natural resources can be considered only by overcoming strong competition from pests, diseases and weeds. Uzbekistan has a long history of using beneficial insects for the pest control. Plant Protection Committee became operational in the first half of the twentieth century. In the early 70's, the regulations aimed at the development of biological and integrated methods of plant protection were adpoted. In Uzbekistan, the Integrated Pest Management is widely used. The essence of the system is to recommend, in phytosanitarian conditions the use of one or another method of pest control which would provide full protection from harmful cultural effects and promote agro-ecosystems. Integrated Pesticide Management is consisting also in agro-chemical, agro-technical measures and biological methods. The role of the chemical method is not excluded, in some cases it may be only way to protect plants from pests.

Key words: entomophagous insects, biofactories, biological and integrated methods of plant protection, IPM

Introduction

Uzbekistan is the second largest country in Central Asia and the first by the number of its population. Agriculture has always been a major component of the Uzbek economy. Cotton and wheat are the most important farming cultures in Uzbekistan, followed by gardens, vineyards, vegetables, melons, potatoes, beans, rice and maize. In the past, the pest control in Uzbekistan, as well as elsewhere, was carried out by chemical methods. However, the widespread use of pesticides has caused irrepairable damage to the environment which are as follows:

- contamination of water basins,
- dramatic reduction of useful entomophagous insects and other animals and plants
- environmental degradation in rural areas
- incidence rate among the population.

In the early 70's, the first biofactories for the production of biological material for agricultural purposes had started (Fig.1-2).

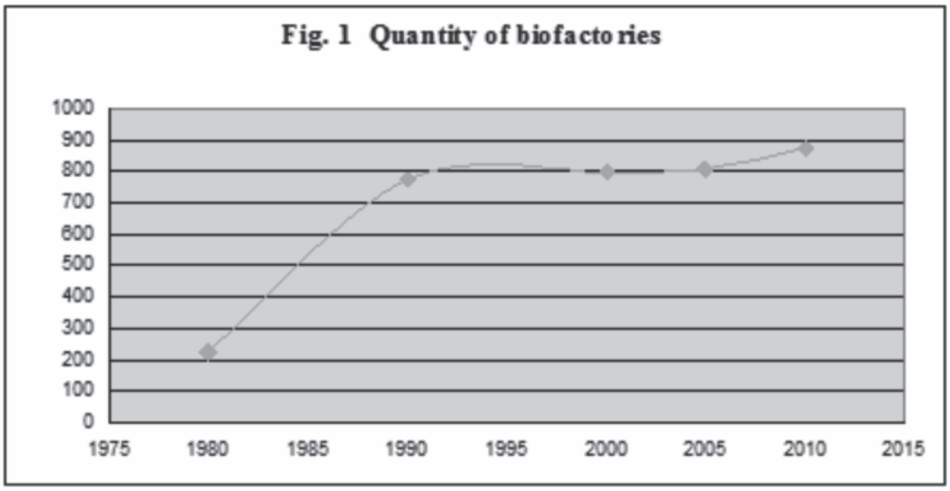
The Republican Central Laboratory "Biosifat" (Bioquality") and its subsidiaries, available in all regions of the country, have been created in order to exercise control over the quality of products manufactured in laboratories and comply with the requirements of the production of entomophagous insects in biolaboratories.

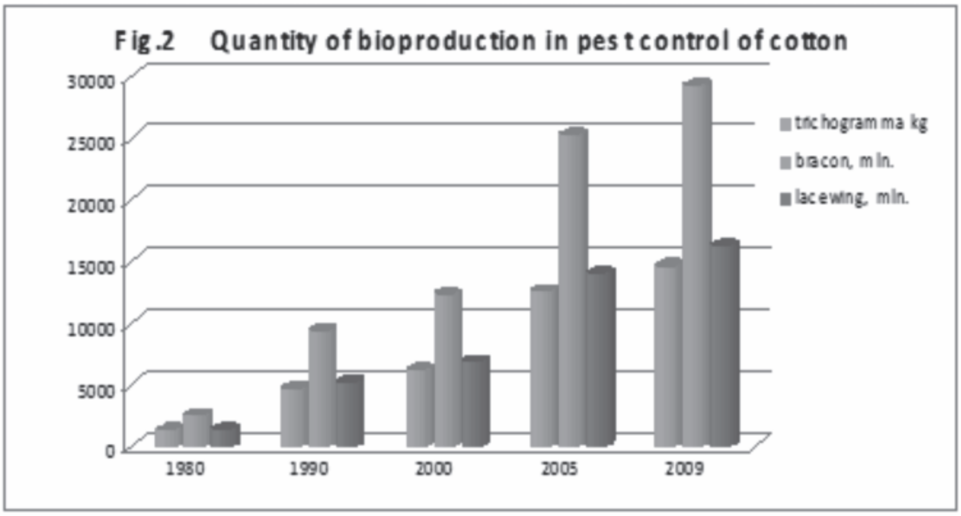
In Uzbekistan, the Integrated Pest Management is widely used. The essence of the system is to recommend, in phytosanitary circumstances, the use of one or another method of pest control which would provides full protection from harmful cultural effects and promote agro-ecosystems.

Advantages of an integrated system (IPM) consist in the fact that it does not completely destroy the harmful organisms and bring them to a safe number for the crop. In other words, the aim of the mentioned system is to provide the cost-harmless amount of injurious insects as food for the entomophags and acarifags in agrocoenosis. IPM is the plant protection system by natural insects which can exterminate the pests.

However, the Integrated Pesticide Management also consist in agro-chemical, agro-technical measures and biological methods. The role of the chemical method is not excluded; in some cases, it may be only way to protect plants from pests.

A special role of the Integrated Pesticide Management is performed by the biological





methods, as the most environmentally safe and cost-effective. For example, the cost of chemical treatment is US$ 9-15 per hectare, whereas the cost of biological methods ~US$ 5 per hectare.

One of the positive aspects of biological method, according to specialists, is the lack of pest resistance to entomophags. As we know, many pests have acquired resistance against the pesticides.

The pheromonitoring insect development methods are also widely used in the country. On cotton plant the pheromone traps are successfully used to indicate the timing of the generations (hence, the timing of the entomophag issuance) and the density of pests. The use of pheromone traps in cotton can reduce the cost of protecting plants from pests by 30-40%.

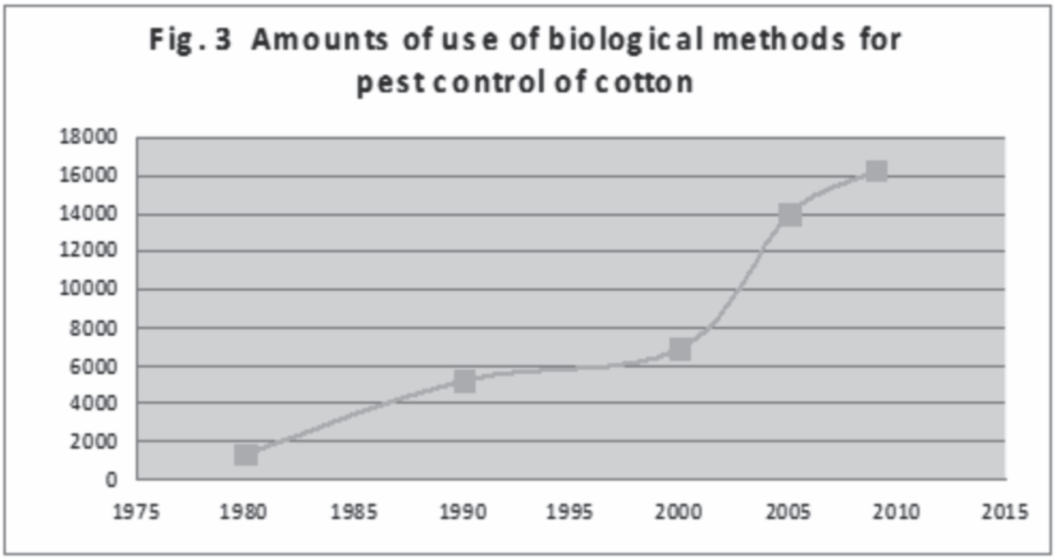
Advantage of IPM

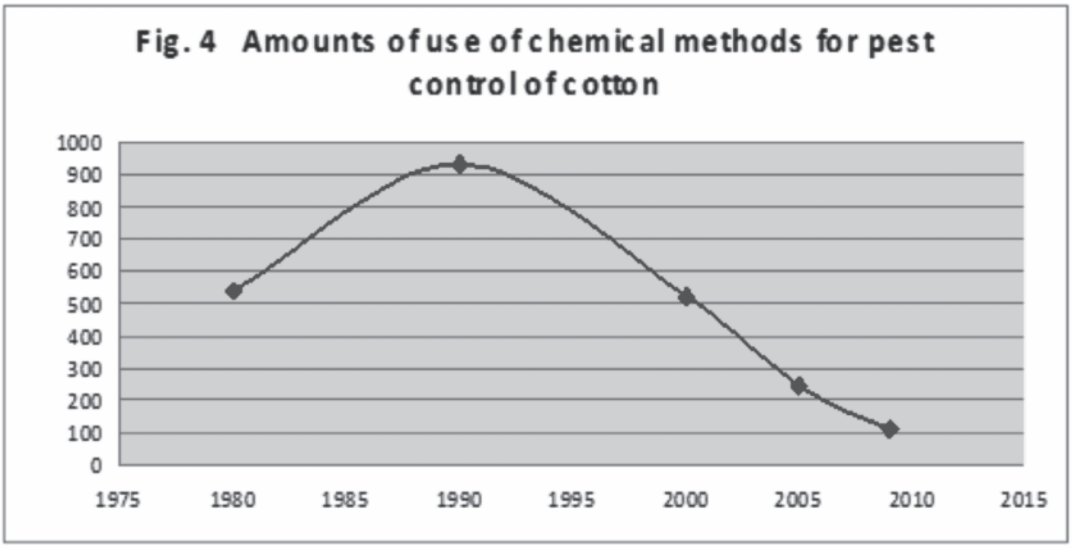
The application of developed technology for integrated agricultural protection reduce usa of crop protection chemicals and save a significant annual investment made by the country for the pest control (Fig.3-4).

The spread of biological pest control methods in recent years has reduced the volume of chemicals used per hectare.

The incidences of chronic poisoning of farmers, during application of crop protection chemicals, have also been reduced. According to the Ministry of Health of the Republic of Uzbekistan, since 1995, there have been almost no cases of acute poisoning or deaths among the employees using chemicals for the crop protection. Over the last five years, there have been only 14 - 30 cases of acute poisoning reported in the country.

In the samples analyzed at the sanitary-epidemiological laboratory of the Ministry of Health, there has been found only one percent of the substances which exceeded the limit of pesticides. In the food, this figure is represented by about 0,3% - 0,7%.





Important role in reducing pesticide treatment is performed by resistant crop varieties which constitute one of the core elements of the integrated plant protection. Populations of pests on the resistant crop are 30-100 times lower than on the susceptible one and the use of pesticides is respectively less.

Conclusion

The nurture of the healthy plants, the use of high quality seed material, timeliness of sowing, harvesting, and seasonal work on the processing of crops - all of these methods of agro technology deliver from the need for excessive chemical treatments of crops.

According to the experts of the National Scientific Research Institute of Plant Protection, sometimes the losses of the crop, caused by the pests, have represented a quarter of crop production. The use of the Integrated Pest Management has allowed saving the crop.

The Government of the Republic of Uzbekistan is taking all feasible measures to develop the Integrated Pest Management in the country. In order to improve the quality of agricultural crop protection, the plant protection service, the efficiency of protective measures, several documents were adopted by the President and the Government of the Republic of Uzbekistan.

Public administration and control of plant protection is carried out by the State Committee for Plant Protection and Agricultural Chemistry under the Ministry of Agriculture and Water Resources, the State Sanitary and Epidemiological Service of the Ministry of Health and the State Committee for Nature Protection of the Republic of Uzbekistan.

THE ROLE OF STEWARDSHIP IN PESTICIDE RISK REDUCTION – A SYNOPSIS OF TWO SUB-REGIONAL WORK-SHOPS

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**** Opinions expressed in this article are entirely those of the author***

Abstract

Pesticides are important tools that help increase agricultural production, improve food quality and safety,contribute to the public health and protect the environment. Effective and fully operational systems that ensure safe handling, use and management of these products are often scarce or weak in most developing countries. Misuse, mishandling and mismanagements of these products continue being significant challenges to these countries andeasy access to the market by banned, unregistered and old pesticides exacerbates the problem. Pesticide consumption in these countries is estimated less than a quarter of the global pesticide production, but more than half of the poisonings and close to three quarters of fatalities associated with pesticide misuse worldwide occur here. This is a clear manifestation of the weaknesses of the pesticide delivery systems partly attributed to lack of adequate knowledge and appropriate skills and scarcity of resources. Limited human and material resources and lack of strong and enforceable regulatory policies and procedures undermine the situation. In countries where enabling work environments and policy directives are absent or rudimentary, societal motivations and creativity are rare and communications among partners are stagnant. To address these chronic problems effectively, a strategy that espouses stewardship through broader participations and collaborations among various stakeholders was developed and tried in two sub-regions. The strategy was focused on strengthening the existing national pesticide delivery systemby promoting, encouraging, and advocating for enabling environments and facilitating broader engagements among stakeholders, including the ultimate beneficiaries.

Introduction

Agriculture employs half of the world's labor force. Nearly a third of the 1.3 billion men, women and children that work in agriculture are paid laborers (PAL)(FAO-ILO-IUF 2005). .Agriculture is the number one consumer and abuser of pesticides and is the most dangerous jobafter construction and mining. PALs in DCs often carry out agricultural activities, including handlingof toxic pesticides, without appropriate protection.

(photo: courtesy of Mr. Zebdewos Salato).

In DCs large quantities of obsolete and toxic pesticides are present (most of which have been banned in developed countries or have limited and restricted uses). In these countries, pesticides become obsolete for many reasons: lack of well planned importation, overstocking for fear of uncertainties among end users, aggressive marketing, forced offers from government sources or associated business partners, poorly assessed donations by benevolent foreign entities and many more.These old stocks cost national governments and donors millions of dollars in clean up and disposal.

While all of these factors play a role in causing pesticide related problems, the solutions to the problems do not seem to match the problems. Strengthening and improving the existing pesticide delivery system (PDS) at the national and regional levels, building capacityand raising awareness among stakeholders and partners can bring some relief to the problem. To address this chronic problem in a more coordinated manner, a strategy that espouses stewardship through active collaborations among various stakeholders was developed under the rubric of pesticide [stewardship] program (PSP)and launched in two sub-regions. The strategy was aimed at strengthening the existing national pesticide delivery systems (PDS) by promoting, encouraging, and advocating for enabling policies and environment and facilitating broader engagements among stakeholders. It emphasizes on sharing knowledge, information and skill among partners, including beneficiaries as well as encouraging mutual benefits of the outcome of the initiatives.

The effort is to get end users from the left photo to right photo (Photo: courtesy of Mr. Salato)

Goals and Objective

The primary objective of the pesticide stewardship networking program (PSNP) is to develop and execute PSP strategies that will improve pesticide delivery systems (PDS) and ultimately achieve the overarching goals of the program, i.e., to minimize human health risks, reduce environmental contaminations, contribute to the national economy and improve well-being of the citizens.

Pesticide Stewardship Networking Program: An overview

Introduction of PSNP as a strategy to improve PDS is one of the strategies widely perceived as an important tool to address thebroader issues of pesticide related problems. The PSN program requires a strong conviction in behavior changes across a spectrum of stakeholders to help reduce pesticide risks to humans and the environment. Fundamental changes in behavior among pesticide handlers, users, regulators, providers, petty vendors and others are necessary in improving PDS and enhancing the execution of corruption-free and effective enforcement of regulatory procedures and policies.

The PSNP strategy emphasizes the creation of synergy among plant protection staff, health officers, environmental practitioners and regulatory bodies and others and strives to lay the foundation for a safer and sustainable use of pest control tools and agricultural and public health pesticides. To attain these, the program advocates for active engagements by partners in disseminating knowledge and skills through all available means. The strategy underscores the importance of launching structured and target-oriented awareness raising and advocacy initiatives for the success of the program.

The PSNP can serve as a process for coordinating and supporting proper disposal of obsolete and dangerous pesticides by exploring and introducing effective and safer alternative pest control tools that can minimize unnecessary use and accumulation of obsolete stocks while guaranteeing effective control and prevention of target pests.

PSN: implementation framework

Effective implementation of the overarching objectives of the stewardship initiative would require a coalition of stakeholders and a public-private sector synergy. Such strategy can be implemented through a well defined and executed program.

The PSN approach stimulates and encourages pesticide experts, regulatory authorities, non-governmental organizations, private sector, researchers, academia, end-users and others to engage in a continued dialogue. It believes that engaging in effective dialogue can significantly improve information flow between and among all partners as well as narrow down the gaps between the source of know-how and skills and the needs among beneficiaries. More importantly, it will help reduce and mitigate pesticide related health risks as well as poisonings and fatalities by enhancing awareness in safety and well-being of producers, consumers, handlers and others. The process will also contribute to protecting the environment and conserving the much needed natural resources. In addition, PSN can help avoid duplication of efforts by optimizing resource utilization, employing integrated production systems and there by contributing to the overall food security and the national economy.

The PSN strategy and its programmatic elements are implemented through the existing structure in the agriculture, public health, and other sectors relevant to its core messages and overarching goals and objectives. Engaging public and private sectors will not only help improve the stewardship education and training programs for the various sectors, but also creates a viable synergy between and among the key stakeholders that play a crucial role in forging ahead a strong and viable PDS at the national, sub-regional as well as regional levels.

The Three Step Approach

Following the above mentioned strategies and tactics, two sub-regional workshops were launched in 2008 and 2009 in East Africa and the Horn of Africa, respectively. The workshops led to the creation of the nuclei of two PSN associations in the sub-regions, leading up to an official registration of a not-for-profit professional association with a regional undertone in one of the sub-regions (Belayneh, 2008, DLCO-EA, 2009).

In both the East Africa and the Horn of Africa initiatives, the creation of the PSN nuclei involved a series of events through ***"the Three Step Approach (TTA)"***. This approach began by launching a series of exploratory consultations with key stakeholders. The consultation processes were focused on needs assessments and interests of host-organizations and other partners. Each step was executed methodically and chronologically. The exploratory consultations took place through a series of direct dialogue with the national authorities that play a greater role in the national pesticide delivery system. The consultations paved the way for an intensive pre-workshop seminar.

Elements of stewardship processes

Key elements of the stewardship process were elaborated and thoroughly discussed and rigorous exploratory activities were undertaken at the pre-workshop seminar. Needs assessments and resource identification at the local, regional and international levels were executed at the seminar. Dates and time for the final workshop were discussed and determinations were made.

The pre-workshop seminar was tailored to give key participants the opportunity to exchange ideas, opinions, and questions which helped define the role of the stewardship within the targeted sub-regional context. It also served as an ideal venue for identifying means and ways to help improve the existing PDS. Areas relevant to and crucial for the implementation of the stewardship were outlined, examined, discussed and defined.

While the execution of all these events was essential, the launching of the sub-regional workshop was the culmination of the processes defining the establishment of the corner stone for the stewardship system. As the prelude to the workshop, individuals and offices were assigned to further elaborate the findings of the seminar. Intensive consultations were undertaken to pursue the coordination and organizational aspects of the stewardship workshop. During this time, significant efforts were made to bring together key players to dialogue and contribute to the findings of the consultation processes and the analysis of the seminar to determine the launching of the workshop.

Operational Themes and Processes

As mentioned earlier, the launching of the stewardship workshop revolved around three primary operational themes using the TTA (DLCOEA, 2009):

1. Developing practical and implementable PSN program,
2. Analyzing needs assessments through the first two steps of "the Three Step Approach" and custom tailoring mechanisms for knowledge and skills transfer at all levels
3. Launching enhanced and improved communication systems that traverse non-traditional domains

The thematic operational teams were formed during the initial period of the workshop and immediately engaged in the analysis and critiquing of the existing PDS. Each thematic group was tasked with discrete responsibilities to further develop its voluntarily mandated sector and contribute to the implementation of the PSN strategy. Each group was instructed to roll out its operational plan for intense discussions by the panel. This process was deemed necessary and proven effective and useful in refining the work plans and making the plans ready for adoption at the national and sub-regional levels.

As per the agreed up on procedures, the program development group focused on formulating procedures and guidelines, drafting by-laws for the stewardship program and defining code of conduct for its operational policies. Likewise, the knowledge and skills transfer group concentrated on formulating relevant means and ways of developing tools and methodologies for knowledge imparting processes and procedures. This group was charged with exploring ways and means of developing training materials, awareness raising and ways and means of ensuring readiness and delivery of these tools.

The communications system and outreach group was charged with developing methodologies, standard procedures and mechanisms for promoting and introducing PSNP to the broader audience and also encouraging stakeholders to join the program or be associated with it. Raising awareness and advocating for safer pesticide handling and use to ensure human health safety and environmental protection were also tasked to the communications system. All of these were carried out within the framework of stewardship process with a clear message of improving and enhancing PDS at the national, sub-regional and regional levels and establishing the descending hierarchy within these structures.

Chronology of observational readout on the TTA mode

I. The First Workshop on Pesticide Stewardship Networking - The East Africa Sub-Regional Experience

The first ever pesticide stewardship workshop was launched in Tanzania in May, 2008 as the East African sub-region [stewardship] initiative. As discussed elsewhere, a dialogue was initiated on PSN with potential partners in 2001 and a pre-workshop seminar was launched in 2005 in Tanzania. Thereafter, the first ever workshop on PSN in East African was conducted in 2008. The sub-regional workshop culminated at the creation of the nucleus of the PSN Tanzania through a 3-step approach (Belayneh 2008).

The workshop greatly benefitted from

collaborative efforts among U.S. Office of Foreign Disaster Assistance's (USAID/OFDA), emergency pests and pesticide program (AELGA), U.S. Department of Agriculture (USDA), various national ministries in Tanzania, Kenya and Uganda, NGO's, academia and others. Full participation by Kenya, Uganda and of course, the hosting nation, Tanzania gave the workshop a great sense of sub-regional endeavor. Added to this, the former Tropical Pesticide Research Institute (TPRI) that once had a jurisdiction over all pesticide related activities in the then East African community played a crucial role and was one of the major attractions for the launching of PSN in Arusha, the hometown of TPRI in Tanzania. Although the establishment [TPRI] has since retained its acronym, it had gone through a name change to reflect its national ownership, hence, Tanzania Pesticide Regulatory Institute (Belayneh, 2008).

The East African sub-region pilot program was able to create the nucleus of the first ever PSN in Tanzania and the region. As a result of the execution of the three-step processes, namely extensive exploratory consultations, intensive dialogue and pre-workshop seminar and the all-inclusive sub-regional workshop, there is a great expectation for rolling out of dozens of networks of trained PS persons equipped with experienced training skills and knowledge. In addition, production of robust and custom tailored training materials is expected. Countries that were represented at the Tanzania PSN workshop have been encouraged and expressed interests to forge ahead with the creation of national level PSN programs and sow the seeds for similar initiatives in their respective regions.

Relevant National ministries, international and regional institutions such as the International Center for Insect Physiology and Ecology (ICIPE), the Desert Locust Control Organization for Eastern Africa (DLCO-EA) and others to which pesticide is an important issue, are encouraged to play a significant role in the development and roll-out of the PSN programs in their respective region.

II. Workshop on Pesticide Risk Reduction through Stewardship – Experience of an Initiative in the Horn of Africa Sub-Region

Work continued in 2008 to establish a similar structure in the Horn of Africa sub-region. In the Horn, the PSN process was initiated through collaborative efforts among OFDA, USDA, DLCO-EA, the UN Food and Agriculture organization's Commission for Controlling the Desert Locust in the Central Region, various national ministries, non-governmental organizations, academia, research, private sector, and other stakeholders (DLCO-EA, 2009).

During the course of the launching of the PSN program in the Horn of Africa sub-region, some fundamental procedures similar to those employed during the Eastern Africa PSN initiative were repeated. Among these were, the launching of needs assessments through the TTA, the development of an implementable PSN program and the establishment of a clear line of communication traversing non-traditional domains.

As in the East Africa, the PSNP initiative in the Horn of Africa started with countless exploratory consultations, dialogue and discussions as well as a number of face-to-face meetings and a pre-workshop seminar. These processes were followed by five days of intense workshop which attracted partners and stakeholders from number of neighboring countries in the Horn, including Djibouti and Sudan (note: despite the fact that invitations were extended to Eritrea and Somalia, participants were not able to join their colleagues at the workshop).

In the Horn of Africa sub-region, the initial process goes back to early 2008 when informal consultations were carried out between OFDA staff and overseas partners and the final workshop was launched in August, 2009 and gave birth to the nucleus of the PSNP. The PSN nucleus has since evolved to become a full-fledged association after receiving an official registration status in June, 2011 in Ethiopia. The official registration of the PSA is the fruit of unabated and unwavering commitments and dedications of members of the executive committee of the PSN and its partners, including overseas sponsors. The association is now recognized as a registered not-for profit, non-governmental professional association under the name: Pesticide Stewardship Association–Ethiopia (PSA-E). Through these steps, the status of the PDS in each and every member-country in the sub-region can be examined and the importance of institutionalizing the PSN program in improving the existing PDS can be demonstrated.

Comparative analysis of the two sub-regional PSNP initiatives

The observational lessons and experiences from both the Eastern Africa and the Horn of Africa sub-regional PSNP initiatives clearly demonstrated the stark similarities between the PDS in the two sub-regions. The two sub-regional workshops have defined clearly the status of the PSD in their respective regions. Furthermore, they have demonstrated the crucial role that institutionalizing the PSNP can play in improving the PDS at both the national and sub-regional levels. Doing so will not only contribute to but also guarantee building a culture of stewardship through a network of stakeholders in a manner that will guarantee sustainability and continuity.

The existing PDS in many of the two sub-regions shared a great deal of similarities. Some of the most obvious similarities are as follows:

- Pesticide related problems in both sub-regions are as critical as they could ever be.
- Lack of adequate resources and weak enforcement capabilities are very much similar in both regions.
- The level of disconnect between the pool and sink of knowledge, skills and expertise in one sub-region is a near-mirror-image of the other.
- There is a critical need for strong hands in monitoring and enforcement of procedures, policies and regulatory standards aimed at improving handling and minimizing misuse of pesticides among subsistence and large-scale farmers and vendors in both regions.
- Counterfeit pesticide products enjoy easy market assess in both sub-regions.
- Stocks of obsolete, unusable and toxic pesticides exist in both regions.
- Diversions of products from intended use to inappropriate and risky businesses are all too common in both regions.
- Communications and interactions among and between key stakeholders, including those that regulate, provide technical inputs, supply etc., are very weak in both sub-regions. To sum up, the problem of pesticide misuse, abuse, and lack of knowledge and resources among the end-users and those that are responsible for monitoring and inspecting of these processes are abundantly evident and the need to intervene and address these problems is very critical.

While the similarities among the existing PDS in the two sub-regions have stark similarities, the differences were, at times, oblique. Among these were thatEastern Africa has a harmonized registration processes, but the Horn does not seem to possess such tool. In depth study of the benefits and cons of the harmonization is beyond the scope of this article, however, it is quite evident that lack of harmonization could encourage unabated movements of illegal and counterfeit pesticides and chemicals. It is to be noted that one of the objectives of the PSNP initiative is to ensure that the cross-border movements of such materials will be eliminated through joint enforcement and policing as well as information sharing.

Conclusion and recommendations

An effective implementation of PSP requires a coalition of diverse stakeholders and a PSN-driven synergy among public and the private sectors, NGOs, research, academia and other sectors. Hence, coalition building should be strengthened among diverse partners and stakeholdersto foster and strengthen PSNP.

Tremendous amount of undiscovered and untappedtechnical skills and knowledge reside within various local, regional, and international organizations and institutions. These are essential ingredients for nurturing the budding PSN initiatives and must be discovered and tapped into.

Strengthening and linking internal and external capacities can improve PDS and significantly improve health and environmental as well as economic benefits. Potential partners and stakeholders should be sensitized to collaborate for a better PSN and such efforts should be pursued to the extent possible.

In sub-regions/regions where pesticide registration procedures are in the process of harmonization or the process is laggingbehind due to a weak coordination among partners, PSN is perceived as an important tool that can play a crucial role by promoting collaborations among partnersby creating a system that straddles political boundaries. Hence this process should be pursued to expedite the harmonization process.

Many developing countries are plagued by free and illegal movements of counterfeit chemicalsacross their porous bordersthat continue eroding their meager resources and adversely affecting the health and safety of their citizens and contaminating their environment. Networking neighboring countries through the PSN can significantly improve policing and halt unwarranted proliferations of such chemicals and thereby avoid the threats they pose to their citizens and the environment. Thus PSNP should be widely and aggressively disseminated among neighboring countries and build a culture of stewardship, i.e., **taking care of something that one does not own**. PSNP partners across political borders are encouraged to actively share information, collaborate with their counterparts and create viable networks and deny market access to illegal chemicals.

Evidence-based programs (EBP) and activities are the key to the success of, not only the PSN-PDS, but also other similar programs and initiatives. This coupled with systematically measuring and evaluating (SME) activities and progress can yield desirable results and have positive and lasting impacts on the way pesticides and other chemicals are handled, used and managed. PSNP should strengthen its EBP and SME processes for better and lasting results.

“Proselytizing” beneficiaries to believe in and own PSN process by laying the foundation for sharing knowledge and entertaining innovative ideas is a huge step forward and an achievement that one should rightfully cherish. Nonetheless, one ought to be mindful of the challenges that lie ahead. One must appreciate the enormous efforts and dedications deemed necessary to establish a fully operational system and maintain the momentum for better and lasting results.

Environmental contaminations like this one are the results of weak policies and enforcement (photo courtesy of Y. Belayneh).

While initiating the PSNP is a good beginning and the right path to pursue, strong commitments and sustainable engagements will remain essential to mainstream the program as part and parcel of the national and regional PDS. Without genuine commitments and dedications, a process or a system will undoubtedly vegetate at the realm of a mental exercise. Bilateral and multi-lateral partners can play an important role in helping lay the foundation, jumpstarting the processes, offering tips and/or showing enhanced generosity, but much of the heavy lifting falls on the shoulders of the national and regional entities. Without them, good beginnings can forever dissipate into oblivion.

The collective vision and aspirationsto make a difference in the lives of the most vulnerable people and communities, including poor farmers, petty vendors, agricultural and health agents, NGOs, educators, the lonesome border control officer and many more can become a thing of the past if coordinated and organized attempts are launched with utmost dedication.

The way forward

Given that PSNP is a high-maintenance initiative, it is important to aggressively promote and sale the idea across different regions by exploring opportunities beyond the horizon. Engaging diverse partners in the PRR processes through regular communications are essential and play a crucial role as part of an overarching stakeholder sensitization. Creating and nurturing the culture of collaborations and information/ knowledge sharing at all levels. Experimenting with the newly created PSA as a guinea pig or a "blue" print for future PSAs and fine-tuning it through the process. Understanding the impact a PSP can have the way communities perceive pesticides and other agro-chemicals, encourage and support community initiatives and empowerment in PDS. UsePSNP to help promote adoption and enforcement of relevant international conventions and protocolsand environmentally friendly policies at the national and regional levels. Maintaining strong commitments and "sustainable" engagements as essential tools for mainstreaming PSNP to help improve PDS at all levels.

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IMPACT OF WINTER WHEAT MIXED SOWING WITH LEGUME CROPS ON THE FERTILITY OF AGROGENIC CHERNOZEMS

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Introduction

For many years, agriculture has been a traditional production area in Azerbaijan. This production area primarily embraces plant-growing and animal husbandry. One of the primary goals of the economic policy of Azerbaijan is to increase agricultural production and improve local food supply chain.Currently grain production is being seen as a high priority for agriculture. Plant-growing accounted for more than 63 percent and animal husbandry 37 percent of the gross agricultural production last year.

It is obvious that soils are still damaged from the use of excessive amount of agrochemicals (fertilizers and pesticides), as well asfrom the heavy agricultural equipments that have been used in order to get high productivity in the agriculture. These synthetic chemicals used in the soil pose harmful effects on the development and activities of soil fauna which ensures natural control of microorganisms, earthworms and pests that are transforming organic residues of plant and animal origin into humus. In general, the use of chemical substances leads to the disturbance of biological circulation of the nutrient elements.

The goal of the research is to achieve effective land use management, prevent soil compression, maintain soil fertility by the use of crop rotation, increase agricultural production by the application of mixed sowing and by improvementof local food supply chain.

Maximum lack of various food substances or nutrients can be observed in the soil without plant cover according to the research findings [3, 4, 5]. Annual losses of nitrogen under different growing conditions were as the followings: without plant – 69.6 kg/ha, crop rotation – 7.0 kg/ha, perennial herbs – 2.2 kg/ha. For that reason, we suggest striped planting method to be incorporated in our research instead of setting the land aside,and thus to prevent wind erosion in the area. Wheat mixed sowing with legume crops in the soil results always in plant cover (even after reaping wheat) and with no negative processes such as losses of nutrients and soil fertility degradation.

Materials and Methods

Description of the research field

Garatorpag farm in Sheki region is located at a height of 350-400 meters above sea level. It extends between longitude 47° 30’ 15.43” east and latitude 40° 47’ 15.06” north. The Neogenic and Anthropogenic remnants are widespread in the area. The annual volume of sunny hours is 2350 hours.The summer months account for 40% of the sunny hours. Through a year the volume of solar radiation is 122 kcal per square cm. The average annual temperature equals 12˚C. It varies between 20-25˚C in July and August. The annual volume of precipitation is 730 mm [1, 2, 7].

Figure 1. Field experiment

Research Methodology

The research was conducted by applying steady field experiment (B.A. Dospexov, 1985). The field experiment was carried out in a grogenic chernozems of "Garatorpaq" rural farm enterprise by striped planting method with 7.2 m spacing between stripes.The scheme and experimental treatments are given below:

1. Background–pure wheat planting+ $N_{60}P_{60}K_{60}$
2. Wheat→wheat→wheat→wheat
3. Wheat+field pea→wheat→wheat→wheat
4. Wheat+melilot→melilot →wheat→wheat
5. Wheat+alfalfa→alfalfa→alfalfa→alfalfa

Close sowing with 7.5 cm space between rows was carried out for all experimental treatments. Sowing norm for additional crops (legume crops)embraced 50% of the sowing norm intended for pure planting in mixed sowing treatment.

The experiment was conducted with 4repeatition for 3 years. The experimental bed area was 216 m^2 (7.2*30).

Results and Discussion

In the research area after two-year rotation the humus percentage based on treatments was relatively different rather than control treatment in agrogenic chernozem soils.According to table 1, the highest humus content (corresp. 5.39% and 3.44%) of 0-20 cm and 0-40 cm layers of agrogenic chernozem soils was observed at the treatment 4 (wheat+melilot→melilot→wheat→ wheat).

Treatments	Soil depth, cm			
	0-20		0-40	
	amount	±	amount	±
1. Background–pure wheat planting+$N_{60}P_{60}K_{60}$	5.00		3.34	
2. Wheat→wheat→wheat→wheat	4.48	-0.52	3.07	-0.27
3. Wheat+field pea→wheat→wheat→wheat	5.12	+0.12	3.38	+0.04
4. Wheat+melilot→melilot→wheat→wheat	5.39	+0.39	3.44	+0.1
5. Wheat+alfalfa→alfalfa→alfalfa→alfalfa	5.25	+0.25	3.41	+0.07
LSD (least significant differences)$_{05}$	0.09		0.04	

Table 1. Impact of winter wheat mixed sowing with legume crops on the amount of humus in soil (2^{nd} rotation), %

This can be explained by having a favourable condition for humus forming microorganisms in the treatment 4 rather than the others. Thus, wheat mixed sowing with melilot results in adequate accumulation of plant mass in the soil, as well as intensive humus forming process for the next wheat planting at the expense of aeration and loosening during soil preparation.

Plant growth and development depends on plant nutrition. Plants produce complex organic substances with the help of solar energy by using simple mineral substances (CO_2 and some salts) and water. High productive and sustainable agriculture consists of agrotechnical measures intended for soil supply with optimum nutrient and water. A significant amount of nitrogen, phosphorus and potassium can be found in the majority of soil. However, the main part of these elements constitutes a form misappropriation or less appropriation for the plants. For instance, nitrogen primarily belongs to complex organic substances (humus substances, proteins etc.), a big part of phosphorus belongs to mineral and organic substances which can not be easily dissolved in water, and a substantial part of potassium belongs to aluminosilicate minerals that can not be dissolved in water.

Soil nutrient reserve is expressed with its potential fertility. Soil ability to ensure high productivity of agricultural plants (for exp. the amount of appropriation forms of nutrients for plants) is the major emphasis on the effective soil fertility assessment.

The impact of leguminous plant cultivation on the amount of food substances in agrogenic chernozem soils was studied. Field pea increases the amount of nitrogen in the soil rather than winter wheat according to the Table 2. The highest nitrogen content (16 times) can be observed at 0-10 cm top layer soil and generally decreased with soil depth. Because round bacteria were more active on this layer. Additionally the amount of mobile phosphorus and potassium in the soil was increased during field pea planting. The notes ofthe increase in the amount of phosphorus in the soil as a result of legume crops planting are described in the literature. Such a fast increase in the amount of nitrogen and phosphorus can be explained by the round bacteria's activity in less productive soils.

Treatments	Depth, cm	pH	Active elements, mg/100g		
			NO_3	P_2O_5	K_2O
Wheat	0-10	7.5	1.8	1.1	36.0
	10-20	7.1	2.7	0.7	25.0
	20-30	7.6	2.0	0.6	19.0
Field pea	0-10	7.5	29.0	2.3	45.0
	10-20	7.4	36.0	1.7	38.0
	20-30	7.6	22.0	2.9	22.0

Table 2. Impact of field pea on the amount of food substances in soil

There is very little information in the current literature about the increase in the amount of potassium in the soil. This can be associated with the soil texture of the research area. Additionally taking into consideration the field pea properties to use not only mobile forms of potassium, but also difficult appropriation forms for the plants (>0.001 mm clay minerals) leads to clear explanation of the achieved results. According to the results of 101 years experience on clay soils in England, plants produce 3-4 times more potassium from the soil together with crop rather than soil reserve of its mobile forms.

Conclusion

The highest humus content was observed in 0-20 cm and 0-40 cm layers (5.39% and 3.44%, respectively) of agrogenic chernozem soils in the treatment of wheat+ melilot→ melilot→ →wheat→wheat after two-year crop rotation in the research area. The impact of leguminous plant cultivation on the amount of food substances in agrogenic chernozem soils was studied. Field pea increases the amount of nitrogen in the soil rather than winter wheat according to the research results. The highest nitrogen content (16 times) was observed at 0-10 cm top layer soil and generally decreased with soil depth. Additionally, the amount of mobile phosphorus and potassium in the soil increased during field pea sowing.

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PESTICIDES RESIDUES CONTROL ON WINE AND APPLES EXPORT

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Abstract

Environmental pollution associated with dissipation of obsolete pesticides, including the persistent organic pollutants, since Soviet era may affect crop yield and its quality. Its increased content in soils may come from more that 424 pesticides warehouses and more than 1000 places, which was used in the past for preparing of treatment solution for agricultural plants; on the other hand, unfortunately, the increase may have an anthropogenic background. Given the fact that agriculture still is, and will remain a major sector of the traditional economy, the Moldovan food products could impose themselves on the international markets due their good biological qualities and safety. Therefore, quality control of agricultural products remains the primary task of the food safety, public health and environmental security in the country into Governmental Program "European Integration: Freedom, Democracy, Welfare" for 2009-2014, Healthcare System Development Strategy for period 2008-2017, National Health Policy of Moldova for 2007-2021, National Strategy on implementation of Stockholm Convention on Persistent Organic Pollutants in the Republic of Moldova, the National Strategy for Sustainable Development of the Agricultural Infrastructure for 2008-2015, etc.

Key words: wine & apple export, a total ban, sample preparation, GC-MS analysis

Task 1. Pesticides residues control in wine. After the collapse of USSR, Republic of Moldova (RoM) lost a large part of its manufacturing sector, including the fact that the country's industrial hub was located in the breakaway region of the Transnistrian Region. Either way, the results was that Moldova was forced to rely even more heavily on agricultural and wine exports.

Actually, the wine industry plays a significant role in the Moldovan economy. Moldova is highly dependent on wine production; it is considered the backbone of the agricultural sector.

The RoM has 130,000 acres (530 km^2) of vineyards of which more than 90% are in private ownership. With its total harvest of 350-500 thousand ton of grapes, Moldova produces 1,2-1,5 million hectoliter of the most prestigious domestic and European wines. Only 15% of the entire production is consumed within the republic, 85% is exported to other countries, which amounts to a sales figure of 313 million USD.

Being a small country with a continental climate and highly fertile soil, Moldova is one of the few European wine producers able to produce a wide range of wine styles.

In global terms, Moldova ranked 7th inoldovan wine collection "Mileştii Mici", with 1.5 million bottles, was included in the Guinness Book, as the largest wine collection in Europe.

The wine industry was estimated to account for somewhere near 25 percent of Moldova's gross domestic product (GDP), with 85 percent of that wine exported to Russia.

In March 2006 Russia imposed a total ban on Moldovan wine based on claims of contamination by pesticides and heavy metals which pose health risk. This financially devastating ban led to losses officially reaching 180 million USD in a country that was already Europe's poorest. Since November 2007 the NATO sponsored laboratory in Moldova plays a significant role in easing re-export of Moldovan wine to Russia. It assists in winery inspections and assists in the imposition of stringent new quality control standards.

According to the Agro-industrial Agency "Moldova-Vin" Moldova exported wine to a number of countries. In the period November to December 2007 export amounted to 99 million USD and in 2008 to 162.2 million USD.

Use of pesticides for protection of vineyards and other cultures against diseases is carried out according to the legislation and of the Republic of Moldova statutory acts and Instructions, namely EU Instruction 91/414 from June 1991. The pesticides to be studied were selected according to testing on the basis of a survey of plant protection products applied by wine and grape producers in the Republic of Moldova. Currently, about 70 active ingredients are registered in the Republic of Moldova for use in the protection of grapes.

In order to enhance food security in the country, the State Center for Certification and Registration of Phyto-Sanitary Means and Fertilizers, equipped with sophisticated equipment to test agricultural products for contamination in the NATO Science for Peace and Security Project 981186 "Clean-up chemicals – Moldova", is authorized by the Government of the Republic to determine residual pesticides in wine, especially the ones for export. The monitoring programmer was carried out in collaboration with about 40 wine producers in three agricultural seasons (2007-2009).

The NATO-laboratory was accredited by the National System for Certification of the Republic of Moldova on the basis of technical competence and independence according to the European

Criteria SM EN ISO/CEI 17025:2006 (Certificate No.SAMDCAECPLI01179 from 23 February 2007). One field of activity of the laboratory is to determine the active ingredients in new pesticides imported into Moldova.

1. IM"Vinaria Bostavan"SRL;	12. IM "Kazayak Vin" SA;	24. SA «Vinaria din Vale & Co» ;
2. IM"Vinaria Purcari"SRL;	13. IM "Shateau Vartely" SRL;	25. IM "Salcuta";
3. IM"Combinatul de Vinuri Cricova "SA ;	14. ICS "DK Intertrade" SRL;	26. SA"Migdal-P";
	15. SA "Nis-Struguras";	27. SA «Vinuri Ialoveni» ;
4. IM "Vismos"SA;	16. "Terra Vin" SRL;	28. «Grape Valley» SRL ;
5. IM "Acorex Wine Holding"SA;	17. SA"Tomai Vin";	29. IM «Basarabia Lwin Invest» ;
6. FCP "Asconi" SRL"	18. SA «Agroniv Bulboaca» ;	30. SA «Leo Vin » ;
7. "Doina Vin" SRL;	19. SA «Euroalco»;	31. «Sem Vin Service» SRL ;
8. "Imperial Vin"SRL;	20. SA «Vinia Traian»;	32. IM «Folicain» ;
9. SA "Fabrica de vin Cojusna";	21. IM «Lion Gri» SRL;	33. SC „Vinaria Tiganca" SRL;
10. SA"Vitis Hincesti";	22. FPC «Aspect Invest» SRL;	34. «Alianta Vin» SRL ;
11. ICS "Suvorov Vin" SRL;	23. SA "Milestii-Mici";	35. SA «Produse Cerealiere».

Table 1. The Moldavian wine exporting companies

The approved methods involve the extraction of pesticides, including the Persistent Organic Pollutants (POPs): DDT (and its isomers/metabolites DDE, DDD), *alpha*-, *beta*-, *gamma*-HCH, Aldrine, and Heptachlor, and also, deltamethrin for the export of wine to Belarus.

Besides chlororganic pesticides, which in the RoM are forbidden more than 30 years back, for export wine in Russia and Ukraine we are testing the fungicides and insecticides that were applied to grapes as metalaxyl, mefenoxam, penconazole, flutriafol, folpet, kresoxim-methyl, triadimefon, triadimenol, cymoxanil, famoxadone, dimethomorph, *alpha*-cypermethrin, and other pesticides.

Reagents and sample's preparation. For identification of some pesticides, are used the analytical standards (> 95% pure) of DDT, DDE and DDD, *alpha*-, *beta*-, *gamma*-HCH, (from Russian origin), kresoxim-methyl, dimethomorph, alpha-cypermethrin ("BASF"), cymoxanil, famoxadone, ("Du Pont"), triadimefon, triadimenol, folpet ("BayerCropScience"), metalaxyl, mefenoxam, penconazole, flutriafol ("Syngenta").

The sample preparation follow the procedure: 200 ml of wine is extracted with Hexane (Dichlormetane, Acetone) in triplicate, dried with anhydrous Na_2SO_4 purified with Aluminium and then evaporated at temperature 40 °C, dissolved in 1 μl Acetone.

GC-MS analysis. Quantities analysis of samples of wine are analyzed using a Gas Chromatograph (GC Agilent Technologies 6890 N) connected with a mass selective detector (MSD Agilent Technologies 5973) equipped with split/splitless programming. The capillary column used is HP-5MS (30 m x 0.25 mm x 0.25 μm).

To avoid some reaction or converting of samples into another substance, helium is used as the carrier gas. Helium with high purity 99.9999% is used at 10.48 psi and a constant flow of 37 cm^3/sec constant flow of 1.5ml/min and total flow rate of 7.5 ml/min.

The temperature of the oven was programmed from 100 °C (hold for 0.5 min) to 180 °C (at 10 °/min), to 250 °C (at 3 °/min) and to 290 °C at 10 °/min (hold for 10 min). The front inlet and detector (MS Quad and MS Source) temperature is 275 °C. The prepared samples were injected 1μl by applying the SPLITLESS.LO programming.

Results

The example of calibration curve for pesticides residues was prepared for concentrations: 1, 2.5, 5, 10, 25 μg/ μl. The retention time of the pesticides is presented in table 2. Example of calibration curve is shown in figure 1.

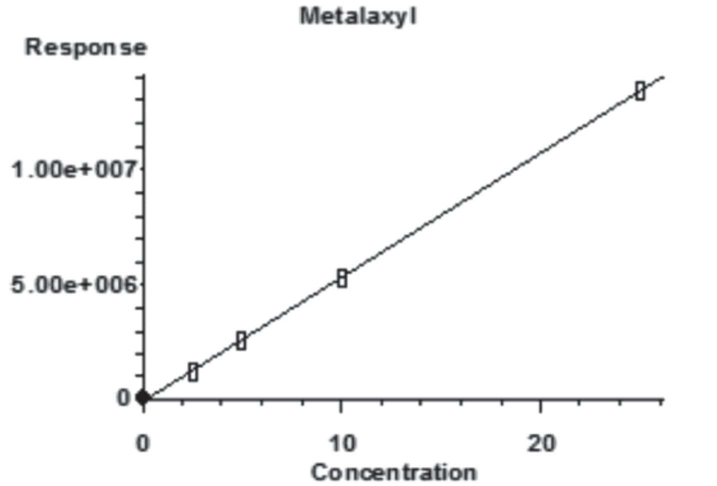

Figure 1. Calibration curve for Metalaxyl

During 2007-2009 *ca* 1000 wine and grapes samples were analyzed. The results obtained show that the POPs (DDT, and its isomers/metabolites DDE, DDD), *alpha*-, *beta*-, *gamma*-HCH, Aldrine and Heptachlor) were not detected. In wine samples of several companies were identified quantities of Metalaxyl and Mefenoxam, which are active ingredients of some modern systemic fungicides, such as Ridomil Gold („Syngenta"), Protexyl („Strand Group Holdings"), Acedan ("Jingma Chemicals Ltd"), Metaxyl („Avgust"). They are applied on vineyards for the purpose of control diseases caused by air- and soil-borne *Peronosporales*. The detected residues of Metalaxyl and Mefenoxam in wine were generally below the Russian Maximum Residue Levels (MRL) for grape (0.03 mg/kg) and the European Union MRL (1.0 mg/kg). (see Table 2).

Task 2. Pesticides residues control in apple

Introduction. Apple is the only fruit crop registering dynamic development in Moldova during the past few years. Since 2007 67.9 ha produced a harvest of 4.88 ton/ha and a total production of 331,352 ton)[A]. Moldova's apple production industry accounts for about 70% of the country's total orchard area. First, the apple industry has a rich research and development tradition. Second, the apple industry is concentrated in the northern parts of the country with higher precipitation rates and a climate unsuitable for other fruit crops. Third, apples are less labor intensive than most stone fruits. Finally, the biological characteristics of apples allow storing and selling the fruit long after harvest.

Apple orchards offer a large variety of raw material for the drying industry. A total of fifty-seven different varieties are grown in Moldova, of which 7-8 varieties are used for drying including some fresh market- oriented varieties. In dried fruit production and export volumes, apples are positioned third.

European Union rules and regulations are strict for trade in food products. The most important ones for dried fruits are the MRLs for Pesticides. The approved pesticide levels in imported fruits are in Council Directive 90/642/EEC (http://europa.eu.int/comm/food/plant/protection/pesticides/index_en.htm). Besides there is the

[A] Moldovan National Bureau of Statistics. 2008.

Approved Additives Regulation which is based on Directive 95/2/EC and deals with the non-nutritive substances, which can legally be added to some or all food products.

Reagents and samples preparation.

A multi-residue method of extraction and gas-chromatographic analysis was done for the quantification and confirmation of 21 pesticides in apple fruits.

Acetone, hexane, and dichloromethane were used for the preparation of stock and working standard solutions, and also in the extraction procedure. The active ingredients of pesticides were obtained from various sources and were of >95% purity (Flutriafol, Lambda-cyhalothrin, Cypermethrin, Azoxystrobin, Difenoconazole (Syngenta, Switzerland), Triadimenol, Tebuconazole, Deltamethrin, Triadimefon, Folpet, Procymidone (Bayer, Germany), Kresoxim-methyl, Dimethoate (BASF, Germany), Diazinon, Captan (***Makhteshim Agan, Israel)****,* Chlorpyrifos (Dow AgroSciences, Austria), Metalaxyl, Phosalone (Ecolan, Russia). The concentrations of the working standard mixture solutions were 1, 2.5, 5, 10, 25 µg/µl.

The original methods were applied [МУ ОМПППКВС, 1992; МУ ОМПППКВС, 2001] as follow: 25 g of the homogenized apple samples was extracted twice with 50 µl mixture of acetone and water (1:1), for 1 h, at room temperature. Following shaking, the sample were clarified and re-extracted (in triplicate) with 40 µl hexane, or by 40 µl dichloromethane, in dependence of target pesticide. The collected extract was then evaporated at < 40°C to dryness, dissolved in a final volume of 1 µl by acetone and analyzed for analytes content by GC/MS method.

GC-MS analysis

Quantitative analysis of pesticide residues were performed using a gas chromatograph (GC Agilent Technologies 6890 N) connected with a mass selective detector (MSD, Agilent Technologies 5973) equipped with a SPLITLESS programming in the same way as pesticides residues control in wine (see in paragraph 1.).

Results

In the period of October 2008- April 2009, 68 samples of apples were analyzed. Samples were collected and represent farms from around the RoM.

The example of calibration curve for pesticides residues in apple was prepared for concentrations: 1, 2.5, 5, 10, 25 µg/ µl. The retention time of the pesticides is presented in table 2. Example of calibration curve is shown in figure 2.

As results of our work, *ca* 10% of total analyzed volume of apple fruits intended for export to Russia was rejected because their high concentration of residual quantities of Chlorpyrifos, exceeding the existent MRL. It should be noted that Russia's standards of content of many pesticides in agricultural products are stricter (lower) than current EU rules and regulations. For example, the

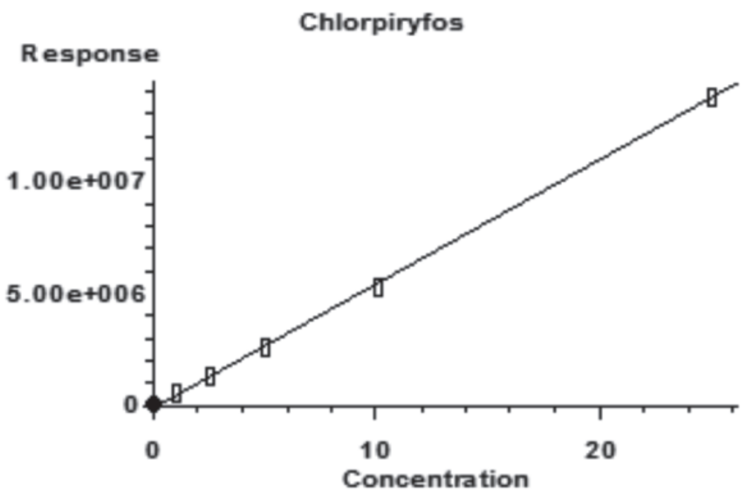

Figure 2. Calibration curve for Chlorpiryfos

Table 1. Retention time, linearity data, MRL (EU/Russian/Moldovan regulations), and typical fragment ions (m/z) of the target pesticides in GC-MS (SCAN) analysis of residues in agricultural products samples (apple, grapes) and wine.

Compounds	t_R (min)	Linearity	Fragment ions in GC/MS (m/z)		Maximum residue levels, MRL (mg/kg)								
			Target ions (m/z)	Confirmation ions (m/z)	EU*			Russia**			Moldova***		
					apple	wine	wine grape	apple	wine	wine grape	apple	wine	wine grape
Diazinon	12,14	0.999979	179	137; 304; 199	0.01		0.01	*n/n*		*n/n*	*n/n*		*n/n*
Chlorpyrifos	15,72	0.999858	197	97; 314; 258	0.5		0.5	0.005		*n/n*	*n/a*		*n/n*
Penconazole	17,18	0.999847	248	159; 213; 186	0.2		0.2	0.2		0.3	0.2		0.3
Captan	17,43	0.999695	79	149; 117	3		0.02	*n/a*		n/a	*n/a*		n/a
Triadimenol	17,71	0.995864	112	168; 128; 57	0.2 *(sum with Triadimefon)*		2 *(sum withTria-dimefon)*	*n/n*		0.05	*n/n*		n/n
Flutriafol	19,08	0.999214	123	164; 219; 83	0.05		0.05	0.1		*n/a*	*n/n*		*n/n*
Kresoxim-methyl	20,78	0.999943	116	131; 206	0.2		1	0.1		0.5	*n/n*		*n/n*
Tebuconazole	24,61	0.998769	125	250; 70; 163	1		2	*n/n*		0.1	*n/n*		*n/n*
Phosalone	28,56	0.993580	182	121; 97; 367	0.05		0.05	0.1		0.1	0.2		0.2
Lambda-cyhalothrin	30,05	0.999503	181	197; 208; 141	0.1		0.2	0.03		*n/n*	0.03		*n/n*
Cypermethrin	34,49	0.998569	163	181; 209	1		0.5	0.05		0.01	0.02		0.01
Deltamethrin	37,19	0.998760	181	253; 77; 209	0.2		0.2	0.01		0.01	0.01		0.01
Azoxystrobin	37,77	0.999091	344	388; 75; 372	0.05		2	*n/n*		0.2	*n/n*		*n/n*
Dimethoate	11,09	0.999400	87	93; 125	0.02		0.02	*n/a*		*n/a*	*n/a*		*n/a*
Metalaxyl	14,27	0.999989	206	160; 132; 146	1		1	*n/n*		0.03	n/n		0.03
Fenitrothion	14,88	0.999630	277	125; 109; 260	0.01		0.01	0.1		*n/n*	*n/n*		*n/n*
Triadimefon	15,67	0.999568	57	208; 85; 181	0.2 *(sum with Triadimenol)*		2 *(sum withTria-dimefon*	0.05		0.1	0.05		0.1
Folpet	17,75	0.999771	260	104; 130; 76	3		5	*n/a*		*n/a*	*n/n*		*n/n*
Procymidone	17.94	0.999977	283	96; 67	0.02		5	*n/n*		0.5	*n/n*		0.5
Difenoconazole (isomer 1)	36,57	0.993759	323	265	0.5		0.5	0.1		*n/n*	0.1		*n/n*
Difenoconazole (isomer 2)	36,68	0.998051											

maximum residue levels of chlorpyrifos in Russia is 0.005 mg/kg, whereas in Europe it is 0.5 mg/kg (see table 2). In conclusion, only 1.5% of the analyzed apple samples did not meet European standards.

n/a - not allowed; **n/n** – not normalized in this environment.

* MRLs utilized database:

- Insertion of MRLs values of Reg. (EC) No 1050/2009 of 06 November 2009.
  substances: Acetamiprid, Azoxystrobin, Clomazone, Cyflufenamid, Emamectin benzoate, Famoxadone, Fenbutatin oxide, Flufenoxuron, Fluopicolide, Indoxacarb, Ioxynil, Mepanipyrim, Prothioconazole, Pyridalyl Thiacloprid, Trifloxystrobin;
- Commission Regulation (EC) No 822/2009 of 27 August 2009 amending Annexes II, III and IV to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for azoxystrobin, atrazine, chlormequat, cyprodinil, dithiocarbamates, fludioxonil, fluroxypyr, indoxacarb, mandipropamid, potassium tri-iodide, spirotetramat, tetraconazole, and thiram in or on certain products;
- Insertion of MRLs values of Reg. (EC) No 256/2009 of 23 March 2009.
  substances: Azoxystrobin and Fludioxonil;
- Insertion proposed MRLs from SANCO document number 4232/2008 Rev 2 voted in March 2009.
  substances: Azoxystrobin, Chlormequat, Cyprodinil, Dithiocarbamates, Fludioxonil, Fluroxypyr, Indoxacarb, Mandipropamid, Spirotetramat, Tetraconazole, Thiram;

** Государственный Каталог пестицидов и агрохимикатов, разрешенных к применению на территории Российской Федерации, 2004, Москва: ОООО «Изд-во Агрорус», 589 стр.

*** Monitorul Oficial RM, 19 Dec.2003, Nr.248-253 (1341-1346).

DESIGNING AND IMPLEMENTING EFFECTIVE PESTICIDE CONTAINER STEWARDSHIP PROGRAMMES

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Abstract

There are two types of container management programmes: obsolete stock *empty* container dispositions and programmes for managing *contemporary* pesticide packaging as each is emptied. The former is usually a one-time campaign that follows the consolidation and bulking of obsolete stocks. The latter, pesticide management or stewardship programme is contemporaneous to the annual use of pesticides. This latter effort is primarily differentiated from obsolete stocks containers in that residue removal is practiced as each pesticide is used. This proper rinsing of containers is neither the sum total of the qualifications for a successful stewardship effort, nor is it even in the early stages of programme development. That success is predicated on a number of decisions and assessments made in an approximate order. Not all of these tools have been provided in previously published guidance. An understanding of the stakeholders and acknowledgement of their motivations are critical in assigning financial and other responsibilities. Producers, users, and the public potentially receive economic or other benefits from proper container stewardship. From this acknowledgement, a return logistics paradigm can reduce environmental health risks by moving recovered packaging to a recycler or other final disposition. Assessing these endpoints include common evaluations for any nation or continent. Once the pathways for returned packaging are set, then the training programme to assure residue removal as each package is emptied is instituted. The author will list additional considerations and provide resources for assuring this residue reduction, return, low risk container stewardship effort is established and sustainably maintained.

Key words: pesticide container stewardship, establishing container recovery programmes, pesticides packaging

Article

There are over 30 nations with pesticide container stewardship programmes. Reliable sources believe that there may be 20 more in just the next five years. Yet, not one of today's thirty plus efforts are identical in structure or outcome. Some are efficient; some are cumbersome. Some are expensive. Several programmes repay a significant portion of the expenses back to the organizers; nevertheless, not one effort is close to self-sufficiency.[1] Some are strictly volunteer industry efforts and others are government mandated or incentivized. In some countries, farmers and other commercial pesticide users cannot imagine business without their container disposal options, while users in other nations grumble about any mandate or quietly ignore the best efforts and continue to discard spent packaging inappropriately.What are the differences? And what more do governments or other stakeholders need to know other than the essential FAO-WHO *Guidance* on Pesticide Containers and CropLife *Roadmap*? [2, 3]

The effectiveness or inefficiencies of any pesticide container stewardship effort are directly the result of the evaluation and implementation process that occurred or did not fully occur at the initiation of this stewardship effort. There are a series of steps that must occur in an approximate order to assure a vital return and final disposition outcome conducive to protecting humankind and the environments. Ignoring any of these steps does not guarantee failure, but not fully addressing each issue does increase that negative probability. What are these steps?

Assessment of the Packaging

The scope and breadth of pesticide packaging is, today, greater than it has ever been. Depending on cropping practices, range of farm sizes, types of public health uses, and so many other variables; pesticide containers can vary from small rigid plastic bottles and even vials up to one-way packages that hold hundreds of litres of liquid or dry product. Although plastics are the predominant packaging medium, their chemistries are not uniform. The resins used in moulding the containers vary all over the map, not only as homogenous constructions, but often as co-extruded and co-blown materials that form virtual sandwiches of materials that at times challenge the recycler's best efforts at reuse. In addition to the ubiquitous rigid plastic containers, there are also thin film or woven bags, sachets, paper bags (usually with another material as a liner), aluminium canisters, gas cylinders, and cold rolled steel drums and cans. Increasingly too, there is also a spectrum of manufacturer or dealer supplied refillable containers and these pose additional stewardship challenges. Although multi-trip containers theoretically address some aspects of material and container stewardship, refillable containers also have stewardship challenges and have a lifespan. Refillable packaging must eventually meet some sort of final disposition.

An early step in assessing a container stewardship programme, therefore, is a national container *inventory* identifying: registrant, type or use of the pesticide, active ingredient, numbers of units, volume, material of construction, and weight of the material of construction. Nations have often limited the use-types subject to container collection programmes. For instance, many collect rigid plastic containers *only* or rigid containers used strictly for crop protection. Others add structural pest and public health vector control, veterinary or seed treatment. An even rarer group have added flexible bags as subject to return efforts. In truth, there are environmental-health benefits to the careful stewardship of all of these packages. If this complete inventory information is not readily available, this *fact* points to the next step:

Regulatory Support or Impediments to Stewardship

There are several regulatory infrastructure deficiencies if container inventory information is not available at the national level. Every compliance agency (or as in most countries *agencies)* need (s) an accurate annual tabulation of all pesticides produced, formulated, or imported into and exported out of that country. A trained cadre of customs officials and producer establishment pesticide officers assure that the data are correct and the labels and contents and packaging are in agreement, and that labels/labeling are in appropriate languages for the users or pictogram supplements are available. This trained staff foils the presence of pirated-adulterated products (and their packaging) as well. Pirated pesticides are a stewardship issue, too. These points are referenced in Articles 5 and 6 of the FAO *Code of Conduct*.[4] Another ingredient in a stewardship oriented registration system is the additional requirement of the package listing, *including materials*, used for each size and formulation of a given product. This point is not directly referenced in the *Code of Conduct* although the code references assessing fees that could, for example, be used for assuring safe packaging ( ), *nor* is it directly mentioned in the earlier Guidance Document for State control of pesticides. [5]. However, the latter document does recommend that the Registrar specify technical requirements for "safe and effective packaging of pesticide". In the same paragraph (4.2.7) the document states: "If the national Government has required approval of the types of containers into which pesticides are to be packaged and offered for sale, there will need to be provisions to the legislation to enable" (this). Changes in packaging must be accompanied by a simple notice to the regulatory agency.

There is one other potential regulatory roadblock to collection and a successful final disposition of pesticide containers. That impediment is the presence of any classification of triple rinsed or the equivalent containers as hazardous waste. Some governments in their haste to implement the Basel Convention on the Control of

Transboundary Movements of Hazardous Wastes imposed "hazardous waste" classification on *all* empty pesticides containers. The 2008 FAO-WHO *Guidance* (Sec 1.5.10) states: "FAO/WHO recommend that countries should classify properly rinsed containers that have been inspected as non-hazardous." [2]

Inventory of Assets

Much is made of the stakeholders in previous publications, so this will not be elaborated other than to say that every nation has the same *classes* of stakeholders: farmers, other commercial users of pesticides, dealer-distributors, the pesticide industry, businesses or even NGOs that could benefit from a return program, and the public good and environment. What is different though is that the relative numbers of each vary and that financial and other intangible benefits of a return-logistics effort can benefit or burden each group differently from one country to another. It is important to analyze these cost-benefits in designing a returnable container effort.

The listing of assets is critical. Exactly what qualifies as a positive ingredient in establishing returnable pesticide programs is as varied as the countries studied. For instance, in some African nations there are state run entities that distribute the pesticides to a specific commodity group: cotton, cashews, coffee as examples. These same organizations are often quite adept at employing reverse logistics to recover the spent containers. The public good is sometimes a more immediate payback than a for-profit distributor. Pesticide retailers also often deliver goods to the customers and return empty. Concerns regarding protection the cleanliness of the vehicle used for deliveries can be overcome using impervious barriers. The presence of highly competitive recyclers can sometimes be employed as collector-processors of spent packaging. A modern cement company in Kenya routinely uses their bagged cement vans for recovering alternative fuels to fire their solid fuel kiln. Final disposition assets (e.g. recyclers or waste to energy facilities) along transportation corridors facilitate economically viable returnable container programs. It is even better if a core group of these facilities can be found as close as possible to the places where containers are used.

Other critical inventory items are to assess the price(s) paid for scrap plastics of the types most commonly employed in regional pesticide packaging. In some instances, waste-to-energy pay for substitute solid fuels and this can also defer some reverse logistics costs. Capacity building expertise in various governmental, non-governmental and even private institutions cannot be overlooked. Understanding how pesticide users get their information on use and application is another important resource. In summary, potential assets and valued information can include: mechanisms for distributing both the pesticides and the knowledge on how to use pesticides, potential final dispositions for various packaging materials (e.g. recyclers, cement kilns) and the financial structure and potential for reverse distributions for each.

Motivator Evaluation

Once the assets and liabilities are tallied (and there are more potential topics listed in both the WHO-FAO *Guidance* and the CropLife *Roadmap*) then one often forgotten step is to determine how each of these assets or strengths versus liabilities or weaknesses impact the 4 big motivators to successful collections for each class of stakeholder (public-government, pesticide industry, distributor-retailer, user group including farmers. The 4 motivators are:

- Environmental Stewardship-the desire to protect the environment for the common good
- Public Health- insistence on zero degradation of worker or health of the population as a whole
- Economics- fiscal impact on individual businesses, classes of industry, or a region or nation.
- Regulatory (or purchasing agreement) Requirement- enforceable command and control insistence on following a certain proscribed course of action.

As an example, if a given area already has a prohibition on discarding individual or large quantities of pesticide containers in landfills and open burning and dumping is enforced, then a voluntary collection effort will certainly collect large quantities of properly rinsed containers. From the economic side, if there are high fees associated with disposal of containers in controlled solid waste facilities, then a collection program will survive and even thrive with no additional incentive. However, if the only motivator is to protect environmental health; it is unfortunately true that only a minority of the users and other members of the private sector will positively respond.

If the economic and command-control motivators are not strong enough to achieve majority participation for each class of stakeholders, then some additional incentive must provide the reason for participation. This additional effort is usually referred to as Extended Producer Responsibility (EPR): the concept that the producer's responsibility never ends when the product is distributed, the resellers stewardship does not end when the product is bought at the retailer or dropped off at the farm or business. It even means that the farmer's responsibility is deeper than growing a commodity. To sell farm products into the richest markets now includes some sort of certification that the grower cares for their immediate environment and this care extends to best environmental and agricultural practices.

This EPR takes many forms, is not uniform, yet all result from the concept: "*if you sell it, you take back*" or, that is, take back any byproducts (e.g. packaging). How EPR is achieved though in every instance involves either mandate (command and control) or economic incentive or both. To date, approximately one third of the pesticide container stewardship programs depend on some form or EPR plus one state in the USA: California. [3]

Implementation and Maintenance

There are examples of differing approaches to establishing container collections on the web. Many references cite establishing pilot programs to flesh out business plans, fairly distribute costs and responsibilities. Other references recommend the selection of schemes for either collecting properly rinsed containers in reverse distribution or some post-use method for baling or other pre-processing prior to shipment to a final disposition. There is no need to review these points again. One area that does warrant some further discussion is how to identify adequate partners for final dispositions. The two most common forms of end use are recycling into products not suitable for consumer use and some form of waste-to-energy. In some rare instances, the only option for non-homogenous packages of little value is proper disposal. Prior to selecting any one of these end points (including disposal), an audit of the potential facility must assure that environmental and worker and other human exposures are minimized. Extremely important is the ability of the chosen facility to keep recovered pesticide packaging under cover in a secure area and assurances that it will not be used or available for unauthorized reuse or remanufactured into future consumer products. Audits usually prescribe engineering alterations, especially for recycling facilities where resin washing is a potential hazard for environmental water contamination. Breathing space air is an issue for workers in and around any heated resin extrusion operation and few recycling facilities have adequate evacuation to force proper fresh air replacement. An example of an audit form can be downloaded at the RobertLDenny.com/stewardship/pesticidecontainer website. Once a facility has been selected and all modifications are in place, a quality assurance program is necessary to maintain these environmental health protections. It is not enough to approve a collaborator *one* time. Follow-up audits are necessary.

The FAO-WHO *Guidance* does address the need for educational programs and lists all of the possible public and private sources for delivering that training. Key points that are not adequately addressed are that the training must begin with both the trainers and the officials charged with compliance. The training must be specific for the locale and local conditions including the sizes and types of containers found in that country. Delivery of instructions are best when in the language of small groups of users who can then each practice the rinsing techniques on non-hazardous mixtures of faux pesticides using household foodstuffs (e.g. milk powder, molasses, powdered maize). An example of adaptable training materials can be found at this RobertLDenny.com/training&education link.

Conclusion

Pesticide container stewardship programmes are a necessary part of pesticide *use.* The employment of this systematic approach began in the wealthiest nations, yet the benefits are just as valuable in every nation, rich or developing. In fact, the environmental health benefits may be greater in nations with little pesticide use. The intellectual and other resources necessary for implementation of a successful program are found through these steps and resources referenced here.

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AN EMERGING STEWARDSHIP ISSUE: LONG LASTING INSECTICIDAL NETS FOR VECTOR CONTROL

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Abstract

Mosquito nets have apparently been around for as long as textiles, but the development of the Long Lasting Insecticidal Net, or LLIN, has brought new hope in the historic effort to curb the scourge of malaria. As new infrastructure and massive resources have mobilized nations to provide "universal coverage" for at risk populations, some concerns have grown that without better end-of-life management, unintended harm to environmental-health may result. In 2010, the WHO Global Malaria Programme launched a Pilot Study in three nations to study the technical, logistical and social or community concerns revolving around the issue of LLIN stewardship. This presentation focuses on just one small aspect of that effort: are LLINs and associated packaging an emerging stewardship issue?

Key words: Malaria, mosquito nets, pesticide stewardship, packaging, pyrethroids, LLIN environmental fate

Introduction

When the fourteen year old Global Malaria Eradication Program was phased out in 1969, this supposedly failed effort did prove that eradication was *feasible* when all of the available resources were brought to bear on disease control. Malaria effectively disappeared in the relatively temperate climates of Europe and North America. Progress was also made in the tropics using the tools of the day[A] in the Caribbean and Central America, though pockets of resistance persisted in Nicaragua and Haiti. In Asia and the Pacific, malaria was eliminated in some regions or the incidence was significantly reduced, as in India and Sri Lanka, only to rise again when the eradication effort ceased. Unfortunately, in Afghanistan and Indonesia there was little progress at all. Throughout this international campaign, the one most afflicted region of the world, Sub-Saharan Africa, received little attention due to post-colonial wars and infrastructure instability in the region.[1] This extreme level of malarial infection was due in the technology of the time or lack of capacity building in the region. Both in the 1960's, as today, Sub-Saharan Africa is home to the most virulent of the 4 malarial plasmodia: *Plasmodium falciparum* and the year-round breeding ground of the most efficient alternative carrier of that plasmodium, the *anopheles gambiae* mosquito.[3]In the late 1990's, almost 40 years after the sentiment was expressed that eradication was impossible, there was renewed hope. Insecticide Treated Nets (ITNs) coupled with an Integrated Vector Control efforts were beginning to show the *possibility* of significant reductions in malaria transmission in discreet areas. In greater Sub-Saharan Africa though, the impacts of the disease itself were worsening. This human tragedy only heightened the world's attention to a continent that was now comparatively more stable as compared to the 3 previous decades. In 1998, these developments culminated in the Roll Back Malaria (RBM) initiative. This WHO effort led to the Abuja Declaration in April, 2000 where 44 of the 50 African malaria infested nations pledged their support and determination to mobilize national resources necessary to combat malaria[3]

A few years earlier, the Long Lasting Insecticidal Net or LLIN was developed, successfully demonstrating that mosquito protection could be achieved over a course of 3 to perhaps 5 years with no retreatment. In these early private applications, the cost was prohibitively expensive for widespread use. It would take

[A]Residual insecticide spaying of homes with mostly DDT, anti-malarial drug treatment, surveillance and mosquito habitat modifications.

Figure 1. Malaria Distribution 1900-2002[2]

large orders to drive the price down to something feasible for RBM initiatives. The only missing ingredient at this point was major sources of funding .The financial resources began to appear, just as there were strong more than just any failings of international interests, commitments from affected nations, and affordable tools for protection if mobilized. Once these key preconditions for effective malarial prevention and perhaps even eradication were in place, the next step was to mobilize net distribution and other integrated vector control measures implementing the WHO stated goal of universal coverage for impacted population. "Universal coverage" is defined as one net for every two persons in an at risk population. Since human populations are neither invariably even in number nor distributed in dual sleeping locations nor are there always static members of every household, effective coverage strategies require dividing the "at risk" population by a factor *les*s than 2. One recent study estimated that number as 1.60[4] and the Roll Back Malaria Program 1.8.

$$\frac{At\ RISK\ Population}{1.6} = Target\ \#\ of\ LLINs$$

Although researchers have used community studies to estimate the number of needed LLINs in a discreet geographical area, the global "at risk" population itself is less of an exact science. One difficulty is the accuracy of census and medical records in some of the areas where malaria is endemic. In 2009, WHO estimated that of the then more than 6 billion people on the planet, approximately half, or 3.3 billion, were either already infected or at risk of contracting the disease.[5] At the close of 2011, with the global population now pegged at 7 billion individuals, it is probable that these numbers of "at risk" persons may have grown due to regional population growth that is at times greater in malaria prone areas than in more temperate climates. Even with population growth, however, the Roll Back Malaria initiative can point to lessening mortality-morbidity data.[2]

What then is "universal coverage" for global populations at risk of contracting malaria? In all probability, net utilization will never reach the level of:

$$\frac{3{,}5\ billion\ Population}{1.60} = 2{,}2\ billion\ LLINs$$

This is a staggering number of nets. At approximately 500 gm/net this mobilization would require the continuous deployment of over a million tonnes of nets. Since nets need replenishment, now thought more likely closer to 3 years than the originally hoped for five years, the world's public health infrastructure theoretically could require replacing up to 700 million nets per year. The potential impact of numbers this large is difficult to visualize. Using an average of specified nets per full size shipping containers,[6]and imagining the containers were stacked in their normal orientation, the one year contribution of nets in 2.59 m high intermodal containers would rise 48,894 meters— over 5.5 times the 8,848 m. height of Mt Everest.[A]Current distributions are not at these levels, but since 2004 until mid 2011 almost a half billion nets[7] have been distributed in Sub-Saharan Africa alone.[B] Any one of a number of promising breakthroughs, some announced just in recent months, could lower that "at risk" population in the future. Examples include: potential vaccines effective against either *Plasmodium vivax* or *P. falciparum,*[8]genetically modifying *Anopheles* mosquitoes to produce sterile offspring[9], or spraying malaria spreading mosquitoes with genetically modified fungi.[10] As heartening as these positive developments are, no one projects that these trends and discoveries will *completely*

[A] Based on fact that 80% of nets are polyester and 20% 40' containers (12.19m length x 2.438 m width x 2.59m in height) to ship a total 560m PES and 140m PE nets equals approximately 18,890 intermodal units.

[B] Number of LLINs distributed by donor programmes, excluding private purchases.

eradicate malaria in the near decade. In effect, there remains and there will remain the need for millions of LLINs as a part of any successful malaria control initiative.

A WHO Led Stewardship Pilot Study

As thoughtful persons absorbed the reality of the sheer magnitude of this historic public health intervention, some scientists and policy makers began to ask probing questions: Are there unintended consequences from net uses other than as malaria prevention while sleeping? What is the environmental fate of spent nets? Are there consequences to unregulated disposal? It was always presumed that there would be some increment of pyrethroids remaining in spent nets. Is the remaining residue significant and do thousands of nets and perhaps more in a given watershed trigger environmental-health impacts? Are there final dispositions for spent nets that also protect environmental-health? If there are acceptable end-of-life (EOL) disposition for LLINs, how should programmes collect and transport nets to those disposal or recycling or energy recovery facilities? And lastly, and most importantly, are their ethical, social, cultural issues that govern the degree of cooperation in releasing nets for collection and EOL management? These are some of the questions that confronted WHO's Global Malaria Programme in 2010 and prompted *Recycling or Disposal of Insecticide Treated Nets used for Disease Vector Control. A Pilot Study in Kenya, Tanzania, and Madagascar*. The study approach divided the overlapping questions for assessment using three research teams: Technical, Logistics, and Community. The three target nations provided input on the same topical areas. Many of the study research and findings are beyond the scope of this brief presentation; however the full report is scheduled for publication in 2012. This analysis will focus only on the preliminary findings related to LLINs as a *potential* environmental stewardship issue.

Nets are fabricated from threads spun from strong polymer filaments. These woven textiles are designed to allow the maximum air circulation while producing an opening that restricts the passage of various species of

A Few Words About LLINs

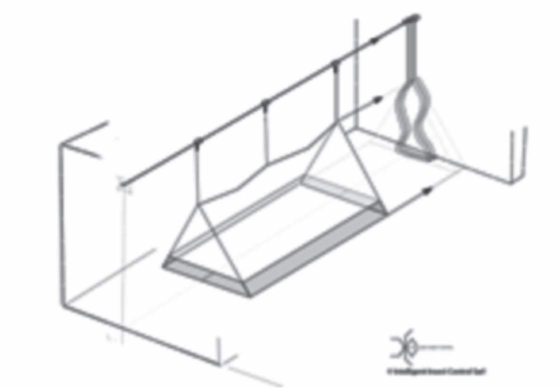


Figure 2. Intelligent Insect Control- design A

Anopheles mosquitoes. LLINs receive their insecticide dosage at different places in the course of fabrication, either before the weaving process or after, depending on the manufacturers' approach. As of today, there are three pyrethroids used for coating or impregnation: permethrin, alpha cypermethrin and deltamethrin.

At the start of this project there were only two types of plastic fibres used worldwide: polyester (80% of all nets) and polyethylene (20% or the remainder of the nets). At least one design employs two different resins in the same net.[11] By the close of this project there was a third resin, polypropylene, used by a new entrant in the LLIN market.[12]Mosquito nets come in any number of different shapes and sizes: conical, rectangular, and A frame. Not surprisingly, the weights of any given design are variable as well. The conventional wisdom is that LLINs weigh approximately half of a kilogram, but some designs may weigh considerably more.

How could nets pose a stewardship issue?

It is not the intended "use" of LLINs that suggests a concern. The mass deployment of LLINs promises one of the most historic victories over this negative degradation to human, social and economic ills ever. Yet, the sheer size of the distributions without an end-of-life strategy raises questions. Manufacturers are required to assess the exposures and risk to humans in an indoor environment as a part of preparation of dossiers needed for WHO approval. It is clear that the risk of low-level pyrethroid exposures to humans of all ages, particularly as compared to the risk of malaria, is more than acceptable. Nets, however, are not required to meet any standards for outdooradaptive uses. And are nets used outdoors?

Figure 3. Gallery of Unintended Uses

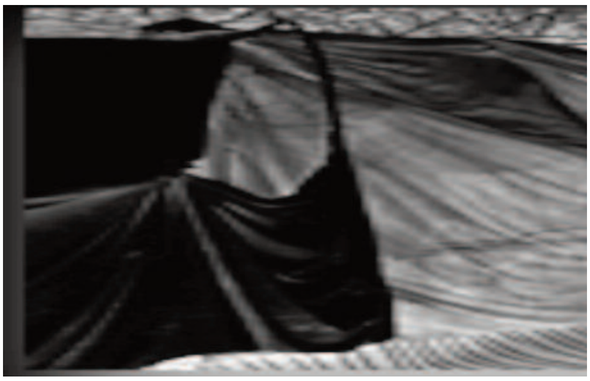
Common Use of Nets as Fence or Screen KE and TZ –M Munga Clltn

Rope woven from LLIN /Net used for Transport

Single almost new LLIN used as Chicken Coop

Images Kenyan Div of Malaria Control unless otherwise specified and single, fairly new net, as packaging -S Hoibak

Single almost new LLIN used as Chicken Coop



Uses as screens-Dadaab KE Refugee Camp- S. Hoibak

From interviews and other information gained by Pilot Study consultants, and 3 country regulators, adaptive reuses lead eventually to uncontrolled disposal. This is the fate of almost every LLIN. Methods of disposal include open burning (most common) followed by burial and open dumping. Although not a part of the original project proposal, WHO did became aware of another issue shortly after the Pilot Study inception meeting. At that time there were only two resins used for constructing nets, three active ingredients, and seven primary producers. Yet for packaging these millions of nets, the manufacturers employed *12 different resins*, plus paper bags and metal strapping.[13] This multitude of materials certainly complicates any effort to recover packaging as a material resource. But recycling of the LLIN packaging is not an option that is practiced or even considered today.

Mosquito net distributions fall into two separate approaches- 1) delivery of nets inside of intact packaging and 2) removal of the net prior to distribution and sometimes even assisting the users in installing the nets in each dwelling. In this latter instance, the packaging is usually collected by the distribution entity and burned. When the nets are left in the hands of recipients,

Figure 4. Net Distributions in Kwale Kenya- Sarah Hoibak

Figure 5. Net Distributions- Region of Madagascar Gaël Du Châtellier

there are reports of adaptive reuses that include, but are not limited to: book bags for school children, food-household storage and other domestic uses. Eventually, like the spent nets, these packages are discarded in an environmentally unsupervised manner.

It is not surprising that packaging of nets have been overlooked as any concern: taken on an individual basis it was presumed that any impact must seem inconsequential. But like the nets themselves or the pyrethroid loading on just one individual net, the impacts can be deceiving. When aggregated, considering that millions of nets are often distributed in a densely populated district or region, an individually small residue, assumes greater proportions when multiplied by numbers with six zeroes. Several of themanufacturer's utilize packaging that weighs just +/-20 grams, excluding the baling and strapping materials. This small mass though. multiplied for every million nets, means that 20 tonnes of packages are almost certainly improperly disposed-again, often in a relatively small area.[13] What are the consequences of this magnified environmental loading?

This WHO Pilot Study sought preliminary answers to these questions using three studies: 1) Identify representative spent LLINs. Using widely accepted methods, characterize the rate of insecticide release through leaching. 2) Assess the potential for transfer of insecticides from LLINs to the envelope packaging. 3) Use established environmental modeling scenarios to assess potential riskspyrethroid transfers to various media in a geographical region.

Leachate Studies

Just finding appropriate LLINs that were identifiably 3 to 5 years of age did prove to be a challenge. Promising leads, evaporated on several occasions due to the stocks being burned. Eventually, stocks slated for a USAID recycling project, were received from Madagascar in Baltimore Maryland USA, then sampled, and shipped half away around the world, past Madagascar, to Intelligent Insect Control'sLabs in Hanoi. This Pilot Study project was scheduled for completion prior to the date when these IIC samples were analyzed.The data were included. The information was too informative to omit.

The experimental design utilized 12 polyethylene Olyset® and 10 Permanet® 2.0 LLINs. Coincidentally, there were 5 samples each of two 2 textile denier sizes of the Permanet LLINs. The first task was to determine how much insecticide remained in each net.Gas chromatography with Flame Ionisation Detection (GC-FID) as specified in the CIPAC Method: 4503/m Permethrin (June 2010) was the selected as the analytical technique. Each net was identified and segmented into samples by JSI Logistics of Baltimore, MD USA and wrapped in foil paper for shipment to Viet Nam. Each numbered sample contained five 35 x 40 cm rectangles of netting: one from the roof and 4 from the walls. Upon receipt, the IIC laboratory cut 100mm^2 circles from each panel to determine the current weight per m^2. A second set of samples were carefully cut as squares from the same netting, cleaning the cutting instrument between net samples. The combined roof and side panel samples were extracted with xylene and used to inject the gas chromatograph. [14, 15]

For the Olyset® LLINs, original weight 500g, at manufacture contained 20 g (+/- 3g/kg) and a cis-trans isomer ration of 50/50 with an outside limit of 30/70. The IIC analysis shows that on average 10.7 g/kg remains although the variability is *large*: 1.4 g-16.8 g/kg. The highest amount, over 83% of the mean manufacturer's weight, was found on the newest net, but the 2nd largest amount is from a net that was 3 years in age at the time of collection. The lowest concentration of active ingredient, 6.84%, was found on the net without a discernable manufacturer's date. The cis/trans isomer ratio is well within the manufacturer's specification across the entire range, indicating relatively uniform isomer decay or leaching rates. [1514]

Ten Permanet® samples were similarly prepared for analysis. All samples had legible Lot numbers. Five nets were manufactured from 75 denier fabric weighing 30g/m^2 and the remaining 5 nets were 100 denier textiles at 40g/m^2. Both have a tolerance of +/-10%[16]

From the IIC Lab data, certain results are consistent with expectations. The 75 denier and the 100 denier nets have all gained weight, but the 75 denier still weighs consistently less (34.91 g/m^2) than the 100 denier textile (45.03 g/m^2). All appear to have accumulated dirt and soiling according to the chief analyst at IIC, Hanoi. In practice, both denier fabric weights are treated with the same dosage per square meter at the time of manufacture. This means that the dosage per kilogram is not the same and the 75 denier textile should have a higher concentration of deltamethrin than the 100 denier fabric. In fact, even after years of use, this is still the case. The 75 denier net has 0.4318 grams of a.i. per kilogram of textile. The 100 denier LLIN retains less or only 0.3122 g/kg.[13, 15]

Since the 2 different textile sizes are dosed at the same rate per area [17], one would expect the quantity per m^2 over time for both textile sizes to be approximately the same. It *appears* that this is the case: 26.2% retention for the 75 denier net and 25.9% for the 100 denier. But the arithmetic mean hides significant variability. The range for the 75 denier cloth is 0.9 -58% retention, and for the 100 denier net: 0 to 80% retention of deltamethrin.[13]

For both Olyset® and Permanet® LLINs, these results indicate that something far more important than age is impacting the quantity of active ingredient retained.

To test for leaching, a standardized wash procedure was carried out on carefully cut, 2 or more, 15 x 15 cm squares of textile from each net.[A] Analyses were conducted using the CIPAC

[A] Details of procedures provided in WHO Global Report.

Method appropriate for the leachate and soil/grime/dirt fractions. Results indicate for all samples from both manufacturers, the amount of dirt or soil adhering to the nets after several years of service is significant. Yet, there seems to be little correlation between the dirt retained and the active ingredient remaining…and hence loss of a.i. /leachate.[13]

If one outlier sample is discarded,[B] eleven Olyset® samples from nets originally weighing 500 g. lost 0.569 g./kg or 5.59% permethrin (range -1.29 > -15.45%).[18]

If one sample is not considered since it is the sample with no discernable peak, then 9 Permanet® 2.0 samples from nets originally weighing 400 g. lost 0.075 g/kg or 23.62% (range -5.08 > 43.84%).[18] Conclusion: even after three to five years of use, in most cases, there are still measurable residues leaching out of nets. More study is needed to understand the huge variability in these data, although pyrethroid leachate, at some level, is almost certainly a reality when nets are re-purposed for outdoor uses.

Packaging Studies

It is a fact that there are an excessive number of different materials used for packaging LLINs. Some manufacturers see little reason to inform WHO or donors when changes are made in the individual net package, baling materials or strapping. Aside from the obvious solid waste questions that this suggests, when you multiply each package by millions there may be other environmental concerns. At the start of this Pilot Study, anyone close to the issue assumed that *some* insecticide was transferred from the net to the packaging. This was not considered a major issue due to the low human toxicity of the pyrethroid class of insecticides. Nevertheless, a decision was made by the designers of this Pilot Study to test the net-packaging interface, not in any comprehensive, industry-wide way, but more as a small sample to see if further study would be suggested. Intelligent Insect Control-SARL, a subcontractor to the Natural Resources Institute (parent institution of the Technical Team), used one of their licensees: Bestnet Europe LTD simply because of their prior relationship. Bestnet manufactures Netprotect®, a LLIN treated with deltamethrin and packaged in PE-PET laminate.

Again, the nets and packages were sampled and analyzed according to international standards[C] on relatively recently manufactured nets and their packaging, stored for 2 months in a warehouse. Analyses determined the total deltamethrin, but importantly the amount of insecticide on the surface of the net and surface and total amounts on and in the packaging. As expected, the packaging absorbed and adsorbed a fraction of the amount of deltamethrin that was both on and in the LLIN [19].

Nets however, are packed 10's of thousands to a shipping container and often take weeks or months of shipping and storage until delivered. The team devised a shorter term 'conditioning' regimen to simulate storage in tropical regions. Some of the designers suggested that this might even be too conservative for the conditions that are actually encountered. Samples were stored in a constant temperature oven @ 54°C for 14 days. Surface and total deltamethrin concentrations were determined for the net surface and the packaging. The heat conditioning did drive the deltamethrin to the surface of the net by factor of 1.7X. But the surprise was the dramatic increase of pyrethroid in the packaging matrix, almost 20X (19.6).[13]Just how significant is this? The total weight of the package is approximately 19 grams. This means that the total deltamethrin content of each bag could

Results: Sample Scenario	Net Surface	Net Total	Pkgng Surface	Pkgng Total
Before heat storage Deltamethrin mg / kg	57.97	1857.62	1.467	2.081
After heat storage Deltamethrin mg / kg	97.47	Not Applicable[D]	5.257	40.876

[B] The smallest permethrin sample, by far, actually indicated a small gain in quantity after washing.
[C] CIPAC method 331/LN/m/4 and other details available in WHO Global Report published 2012.
[D] Data not taken as "new" net usually not considered for disposal/recycling final disposition

range somewhere between 0.038 mg when recently manufactured to 0.78 mg after two weeks of conditioning in an intermodal container in a hot sun.[13] There have been reports of some workers who distribute nets exhibiting symptoms of pyrethroid exposures.[20]Another unknown is the environmental impact of uncontrolled disposal of packages, remembering that the Bestnet product is just one of many packaging-LLIN interfaces. No one is suggesting that this is a Bestnet problem, and the Technical Team appreciated the willingness of Bestnet to supply samples for these test. Instead, this is likely an industry-wide, donor and institutional issue that demands attention. In one very short time-frame, millions of these packages could be disposed either by distribution teams or users, depending on the authority's choice. And packages, unlike impregnated or coated nets, do not release their insecticidal loading over time, but almost all at once. Questions inevitably arise as to unnecessary impacts to both humans and the environment from this one potential source. To their credit, WHO Global Malaria Programme responded swiftly to these revelations and has already published (draft)

Interim Recommendations on the Sound Management of Packaging for LLINs.[A] Long term solutions to this stewardship challenge remain. This task demands attention from everyone involved in malaria programmes. And unlike the more complex questions of LLIN stewardship, no one can credibly claim that the myriad of different resins employed for packaging or even the fact of packaging itself puts anyone at risk if more thoughtful packaging stewardship is implemented.

Environmental Modeling

These three approaches for assessing "if" unintended uses or uncontrolled disposal of LLINs may pose any stewardship issues for humans, and especially the environment, are not in chronological order. Due to the difficulty in finding test samples, the previous two approaches came last. One study, conducted by the Institute for Chemical and Bioengineering, ETH Zurich, is important for illustrating both the potential for harm to aquatic species from uncontrolled disposal/mismanagement of LLIN[B] *as well as* the uncertainty that confronts malaria programme policy makers.

The ETH Zurich Institute conducted an "*assessment of environmental exposure and associated risk from uncontrolled disposal and repurposing for unintended uses of long-lasting insecticide-treated nets (LNs).* (This modeling study) *was conducted by constructing a number of scenarios intended to represent a variety of environmental and use conditions that could be encountered.*[21] These brief excerpts are unquestionably depriving reviewers of this document a complete and comprehensive image of the Institute's findings, yet that in depth analysis is outside of the scope of this overview of potential emerging stewardship issues relative to LLINs. The Institute's work is suitable for a separate, stand-alone presentation. There are two points though, that are cogent to this presentation.

1. The author's wrote: "*Because of the very high toxicity of pyrethroid insecticides to aquatic organisms, it was found that disposal to water bodies was particularly problematic, and most scenarios led to levels in water exceeding published maximum allowable concentrations (MAC).*[21]*"* And what does "disposal" to water bodies mean in this context?

   The Institute used a modeling scenario calculating the pyrethroids released from LLINs using the Small World mode, originally coded by Matt MacLeod. It is a fugacity-based multimedia mass balance box model that describes the environment as a series of interconnected boxes, *compartments*, as they are usuallylabeled. For this discussion it is important to understand that any compartment can consist of multiple phases *or* physical states. For instance, the Air Compartment can contain the obvious

[A] http://www.who.int/malaria/publications/atoz/final_draft_interim_recommendations01nov2011.pdf
[B] Testing had not indicated packaging as a concern at this point.

gaseous components as well as solid or liquid aerosols. Most importantly, for this discussion it is critical to understand that the Fresh Water compartment contains both the obvious liquid (water) phase and all things dissolved in it, but also suspended solids.

Pyrethroids have a remarkable affinity for organic matter and are not particularly soluble in water, hence making them ideal for binding to textiles, for instance. These traits help explain how it is possible for large aquatic ecosystems to have higher concentrations of pyrethroids than chemical-water solubility would predict. The pyrethroids are bound to suspended sediments, plant materials, organic-rich substrates that in rainy wet regions, such as the tropics, can generate run-off from areas where pyrethroids are disposed or used for unintended purposes. Alternatively in drier regions, pyrethroids are at times airborne as dust particles or are suspended only to find their way into precipitation; thus ultimately entering into the Water Compartment. In this case of pyrethroid risk, it is this Water Compartment that is of the most concern.

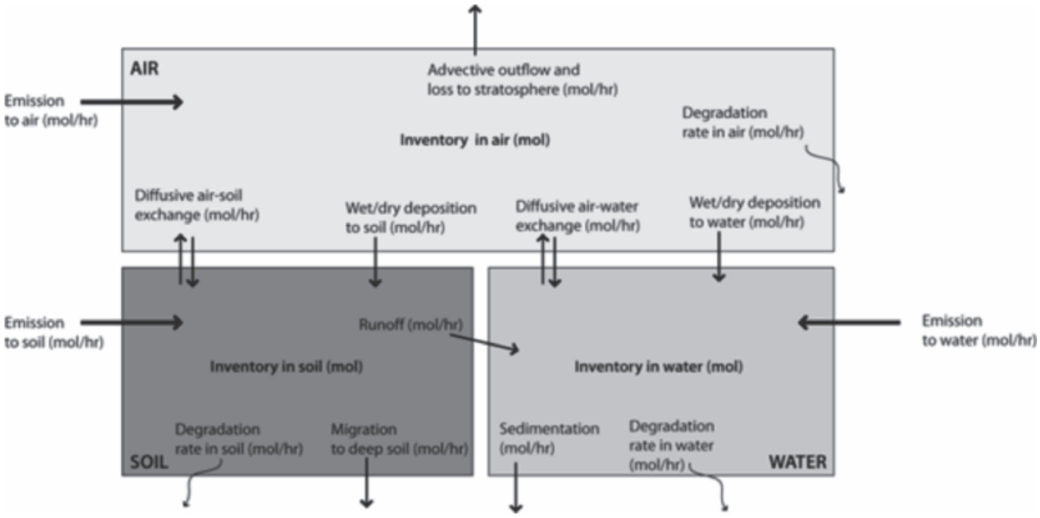


Figure 6. "Small World" model representation.
The inventory is the total mass of chemical present in a compartment at steady state.[21]

2. The authors of the Zurich Institute report also wrote, more eloquently than summarized here, of the dearth of data available to definitively predict with certainty the risk to media outside of the Water Compartment. Topics investigated included emissions to soil, particularly to soil organisms and emissions to crops since use of nets for food storage and protection of crops and foodstuffs is a common practice. There are a number of statements such as, "*there is high uncertainty surrounding the exact uptake of* (pyrethroids) *into plants...*"or "*uncertainty surrounds the estimation of chemical half-lives in the vegetation compartment*" or "*on crops* (internally) *the picture is less clear.*" Also, there are less data useful for modeling newer chemistries like cypermethrin, "*one of the most toxic of this pesticide class*." In fact, the authors said, "*substitution of currently used chemicals* (pyrethrin and deltamethrin) *for more toxic ones, such as cypermethrin—could warrant more elevated* (environmental risk) *concern*." Yet, due to the lack of established models using cypermethrin, most of their scenarios were based on permethrin and deltamethrin.

In their conclusions, the Institute scientists stated: *The uncertainty related to pyrethroid fate in the crop cover scenario is perhaps highest. It is unknown whether a substantial fraction of the AI in nets can be transferred to crop surfaces via abrasion. Further, models of chemical fate within plants are not as well developed as for other environmental compartments, so high* *uncertainties remain regarding distribution and degradation rates. Although it is expected that the amount of AI transferred in this manner will be much lower compared to, for example, direct application in an agricultural setting, it may present a special exposure case, as nets may be used on 'local' (i.e. subsistence rather than commercial) crops where pyrethroids would not otherwise be used. Thus, a closer examination of this possible scenario and field measurements/analysis of transfer to vegetative surfaces may be warranted.*

Because of the deliberately engineered long-lasting properties of these nets, which involve the migration of the AI to the surface, discarded nets may pose particular problems as local 'point sources.' However, this type of analysis is difficult to pursue from a general perspective. In order to better quantify the risks of specific use scenarios for specific environments, a local case study might be warranted,...[21]"

In summary, real data are needed for a definitive assessment of environmental risk, particularly to foodstuffs and crops. However, the suggestion of environmental risk from outdoor uses or unregulated disposal is strong, and when the practice is near or in aquatic systems the possibility of harm is more than a suggestion.

Conclusion

In one short presentation, it is impossible to treat this multi-dimensional topic of LLIN stewardship fairly and clearly. There are so many overlaying concerns. And yet, one must never forget — malaria is a killer. Even now, well into the 21st Century, these tiny *Plasmodia* hop from *anopheles* mosquito to human host and back again and claim the lives of more than 781,000 people worldwide.[22] Uncounted millions more are infected and lessened as contributors to society. Each and every 30 seconds, either while I write this speech or as I deliver it, a child dies from this dreaded disease.[23] No one would suggest any action that might prevent a child or any adult from receiving the protection they need to possibly prevent this mortality or morbidity. Still, we must ask this question: Is it possible to keep this predominant public health goal uppermost in priority *and* minimize any or all unintended consequences to environmental health? If this author did not believe it possible, this presentation would never have been written.

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Figure 7. Image -Vestergaard-Frandsen Brochure

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SESSION 5. POPS MONITORING

RESEARCH CENTRE FOR TOXIC COMPOUNDS IN THE ENVIRONMENT (RECETOX)

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The Centre is an independent department at the Faculty of Science, Masaryk University, with its own research and development, educational programs and expert activities within the field of environmental contamination. The Centre focuses on persistent organic pollutants (POPs), polar organic compounds, toxic metals and their species and natural toxins - cyanotoxins.

The research centre was established as the National POPs centre of the Czech Republic in 2003 and got a lot of experience with transferring of the scientific knowledge into the field of application, executing field and laboratory experiments and measurements to collect necessary information for the implementation of the Stockholm Convention as well as with organizing various conferences, workshops and training programs focused on the capacity building and transfer of knowledge. RECETOX participated in the development of the National inventory and National implementation plan in the Czech Republic and continues to serve as a scientific base for the implementation of the Convention.

Since 2005, the RECETOX monitoring and educational activities spread over the area of Central and Eastern Europe, and endorsement of RECETOX as the Stockholm Convention Regional centre for capacity building and transfer of technology in the region of Central and Eastern Europe was the logical step completing the previous efforts. In this role, the centre advocates the idea of the specialized centers capable of providing technical assistance in, as well as outside their own region.

The Centre offers the strongest expertise in the area of POP analysis ranging from the development of sampling techniques (for air as the key matrix in the Global Monitoring Plan, but also for water, for which the need increases with new and more soluble substances added to the list of SC) and their application in the field, through the development and application of analytical methods (not only) for new chemicals placed on a list of the SC, up to the implementation of pilot studies and long-term monitoring programs, management and data processing and development of environmental databases. Complementarily, the Centre also provides a base for eco-toxicological studies focused on the effect of chemicals on living organisms, the analysis of the environmental and human risks and impacts of chemical pollution on biodiversity.

In these areas, the Regional centre provides technical support not only in Central and Eastern Europe, but also in other regions where such expertise is missing, such as Africa, Asia or Pacific. In these regions, the RC helps with the implementation of the Global Monitoring Plan and execution of the short-term, as well as long-term measurements. Last, but not least, the Regional Centre contributes to regional capacity-building needs. **The International Summer School** organized in cooperation with the Secretariat of the Stockholm Convention and the Ministry of Environment plays a major role. The school is offered (and used) worldwide and represents one of the most important tools for capacity building and the effectiveness evaluation under the SC.

Next important activities in the CEE region are:

MONET EU project that is focused on long-term monitoring of air quality at background locations has been proposed. Given the fact, that there are no consistent data on air quality in most of Europe (with the exception of few EMEP stations), such a large scale monitoring campaign is unique and helps to compare the sites across the continent.

GENASIS (The Global Environmental Assessment and Information System), the expert system representing a new generation of multi-dimensional software for expert analysis of environmental data, was developed by the Research Centre for toxic compounds in the environment into a form that is used to visualize and interpret data from the Czech national inventory updating. The initial phase of the project focuses on data from regular monitoring programs that provide a general overview of spatial and temporal trends in concentration of pollutants in different environmental matrices. All data available on POPs in ambient air of the Czech Republic as well as results of the MONET international studies are currently part of the system. The GENASIS project is driven by the need of having all valuable data on the presence and environmental distribution of hazardous compounds in one database accessible to a wide spectrum of users. Thus, GENASIS was offered to the Secretariat of the SC as a tool for visualizing data reported under the GMP. The Centre is keen to cooperate in its development with other monitoring projects, in order to deliver the most comprehensive information.

Support and measurements in CEE region: In addition to long-term large-scale studies, the centre also support the short-term campaigns in order to obtain the pilot data on contamination of the CEE region.

In Azerbaijan, a single large-scale campaign was performed in cooperation with the University of Lancaster in order to screen the situation with contamination ambient air (by passive sampler), soil and butter in 2010. In Kazakhstan and Kyrgyzstan two UNDP/GEF projects are to ensure minimization of PCB releases and subsequent health and environmental impacts through systematic capacity development for sound PCB management in the countries. The Czech Republic (represented by RECETOX) is seen as a good partner for the projects, because of the country's experience in strengthening and improving national environmental policy and management. The Czech experience in addressing hot-spots and identifying priority areas and sectors for risk assessments, monitoring and clean-up will also be very valuable for Kazakhstan and Kyrgyzstan.

RECETOX also puts a lot of effort into the awareness rising among the professionals, legal state and regional authorities, private companies, students and general public

CENTRAL EUROPEAN AMBIENT AIR ORGANOCHLORINE PESTICIDES LONG TERM TRENDS

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Abstract

Kosetice observatory is a facility of the Czech Hydrometeorological Institute which is a part of European Monitoring and Evaluation Programme (EMEP) network. Now this observatory represents also very important site of the Global POPs monitoring of the Stockholm Convention. Persistent organic pollutants (POPs: PCBs, DDTs, HCHs, PAHs) have been monitored in all environmental matrices using the integrated monitoring approach, which world-wide unique set of data. Data from the period 1996-2010 of integrated monitoring at Kosetice observatory were used in this project to assess long-term trends of POPs in the ambient air in the European continental background.

Generally, the atmospheric levels of POPs in this Central European background station are significantly higher than those in other EMEP stations localized mostly in Northern and Western Europe. Long-term trends of POP concentrations in the ambient air and other environmental compartments show a slow decline in the last years for most of investigated compounds. This is consistent with data reported from other European sites. The long-term background monitoring is an excellent way to study the regional levels and trends and also a powerful tool for evaluation of the impact of various local and regional events – from industrial accidents to natural disasters. This conceptual approach has the potential to play a crucial role in the implementation of regional and global measures and conventions on persistent toxic substances.

Key words: Persistent organic pollutants, long term global and regional monitoring of ambient air

Introduction

Persistent organic pollutants (POPs) represent several classes of organic chemicals including polychlorinated dibenzo-*p*-dioxins and furans (PCDDs/Fs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and other industrial and agricultural chemicals, newly also brominated flame retardants for example polybrominated diphenyl ethers or hexabrombifenyl and fluorinated substances. Also polycyclic aromatic hydrocarbons (PAHs) are often included in this group of compounds because of their potential for long-range transport even though their physicochemical properties do not suggest the persistency and bioaccumulation potential.

POPs including organochlorine pesticides are persistent, with high potential to the accumulation in abiotic environmental compartments, strong tendency to bioaccumulation in human and wildlife and bio magnifications in food chains, with a very broad range of potential harmful and a strong potential to the long range transport round the Globe.

They have been the subject of scientific interest and also the subject of international regulation tools such as international conventions or directives for the last few decades. The most important now are the Stockholm Convention (SC) on POPs and Convention on Long Range transport of Air Pollution (CRLTAP) and its POPs Protocol, the first from the global point of view, the second for the European, regional point of view. Both Conventions developed, adopted and implemented the long-term monitoring programmes.

The effectiveness of the Stockholm Convention (SC) according to Article 16 of the SC shall be evaluated after four years since its entry into force, and periodically thereafter at intervals to be decided by the Conference of the Parties (COP). Global Monitoring Plan (GMP) has been developed with the aim to evaluate whether the POPs actually were reduced or eliminated on the global scale [1,2].

CRLTAP has a monitoring strategy and programme so EMEP (European Monitoring and Assessment Programme). The main objective of EMEP Programme is to provide Governments and subsidiary bodies under the CLRTAP (The Convention on Long Range Transboundary Air Pollution, signed 1979) with qualified scientific information to support the development and further evaluation of the international protocols on emission reductions negotiated within the Convention. Map of the EMEP stations with POPs monitoring activities (including analyzed matrices) is presented in Figure 1 [3,4].

The distribution and number of sites measuring POPs are insufficient, but possibly will the EUs daughter directive on PAHs and the Stockholm Convention on POPs have a positive effect also on the number of EMEP sites. At present, only one observatory from this network is located in the Central and Eastern European region – Košetice observatory in the Czech Republic.

Methods

Sampling site

Košetice observatory (last to the right) was the only site where POPs were/are also determined in other environmental matrices. Košetice observatory of the Czech Hydrometeorological Institute is located in the southern Czech Republic (N49°35´; E15°05´) [5,6]. The climatic classification of the region is moderately warm and moderately humid upland zone with a mean annual temperature of 7.1 °C, mean annual total precipitation of 621 mm, between 60 and 100 days with snow-cover per year, 1800 hours of sunshine per year, and prevailing westerly winds. Observatory was established as a regional station of an integrated background monitoring network in the late 1970s [7,8].

Figure 1. Only six (out of fifteen) EMEP sites reported POPs in both, air and wet deposition, in 2004

All measurements assigned to EMEP stations (including VOCs, POPs and heavy metals) are currently implemented in Košetice [5-8], and monitoring design is based on the EMEP POP monitoring strategy EMEP from 1998. Samples of the ambient air, wet deposition, surface water, sediment, soil and biota, as the key components of the environmental system, are collected. The ecosystem indicators are further applied to determine the current state, anthropogenic impacts and influences, and to predict the future changes of terrestrial and freshwater ecosystems in a long-term perspective. A dataset generated in ten years of integrated monitoring in Košetice was used in this study to assess the Central European trends in background levels of persistent organic pollutants. This dataset is from 1988 produced by the RECETOX, Masaryk University, Brno, Czech Republic.

Sampling, analysis, QA/QC

Selection of compounds, methods of sampling, sample preparation, analysis including QA/QC procedure, were published recently [7].

Results

The results from this observatory represent a very unique set of data [5-7]. The ambient air measurements exist since 1988. But, from 1996 until now, the used sampling and analytical methods are the same and results comparable. It means that we have a set of approximately 800 samples (53 per year) of POPs in ambient air, which in EMEP represents the central European background site. This set is very robust, has a long-term level of information, world-wide unique and represents a very solid base for evaluation of temporal and seasonal trends of POPs in ambient air on the European continental background level.

Concerning to the ambient air levels of OCPs, their profiles and long-term trend are represented in the figures 2-5). Most of these compounds were banned in Europe in 80s and their maxima are not connected to their production or seasonal application. They are present in atmosphere due to volatilization from the old deposits (soils, sediments, wastes) or due to long-range atmospheric transport from the regions where they are still being applied or were frequently and intensively used. In agreement with this hypothesis, elevated levels of organochlorines are observed in warmer seasons when increasing temperatures enhance evaporation of these compounds. This seasonality is not as well pronounced as it is in the case of PAHs, but it can still be detected for pesticides in Figures 2-4 [5-7].

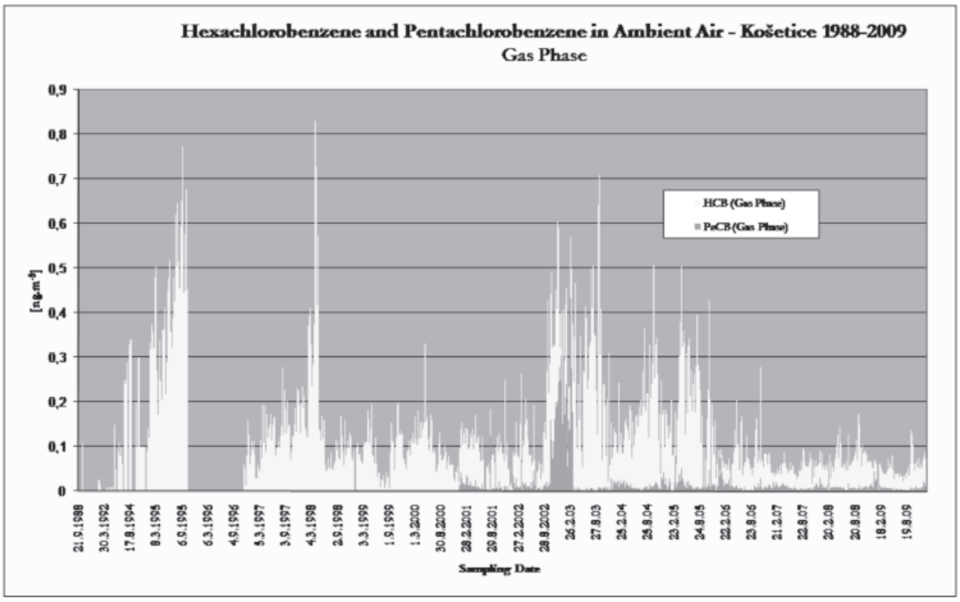

Figure 2. Hexachlorobenzene (HCB) and pentachlorobenzene (PeCB) (determined from 2001) in ambient air (ng m-3), Košetice observatory, 1996-2008 (weekly sampling).

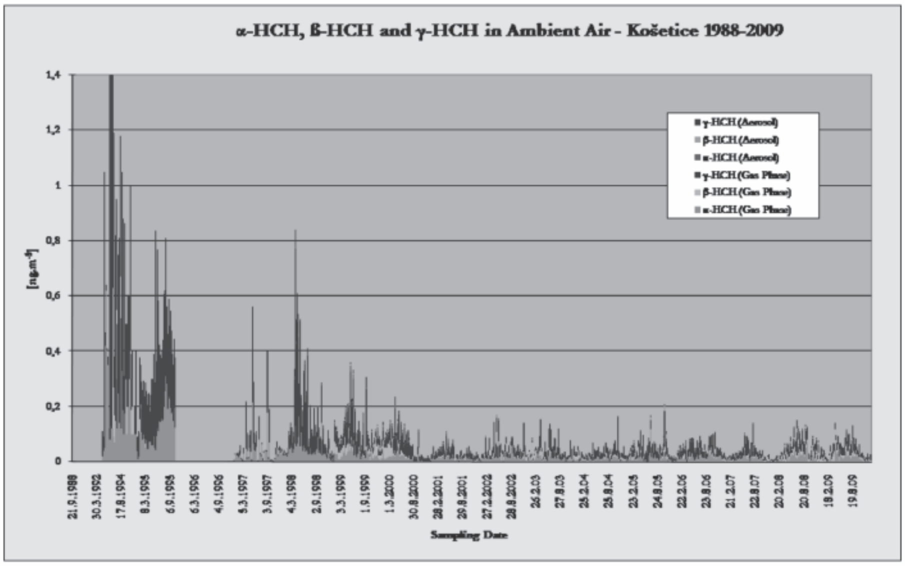

Figure 3. Hexachlorocyclohexanes (HCHs) in ambient air (ng m-3), Košetice observatory, 1996-2008 (weekly sampling).

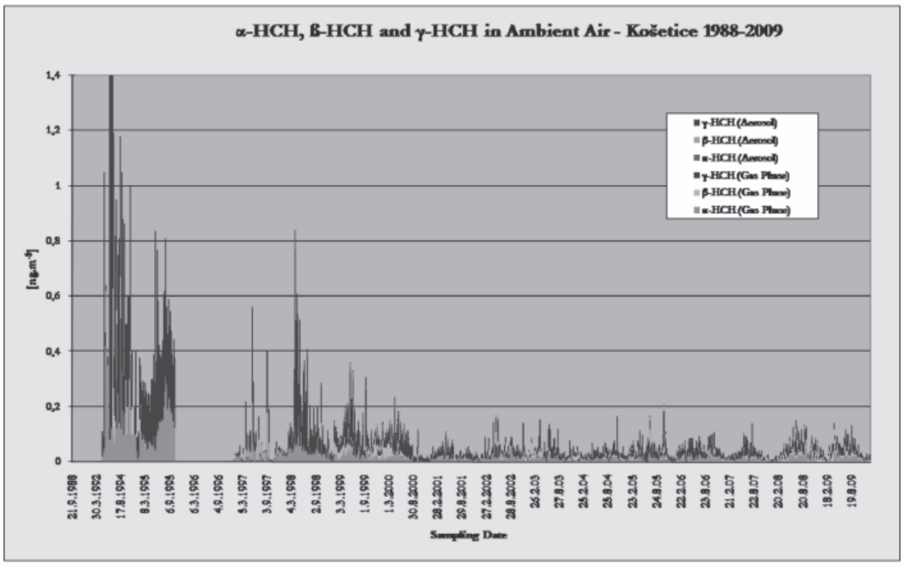

Figure 4. DDTs in ambient air (ng m-3), Košetice observatory, 1996-2009 (weekly sampling).

Annual median air concentrations were calculated for all subgroups (PAHs, PCBs, HCB, HCHs and DDTs) and resulting values were compared to evaluate the long-term trends for each group of compounds in the period of 1996-2008 (Fig. 5). Trends which were presented in [7] continue [2].While PAH levels have been quite stable in the last decade, PCBs showed generally decreasing trends. Pesticides fluctuated showing highest atmospheric concentration in two periods immediately following the major floods (1997 and 2002) [2].

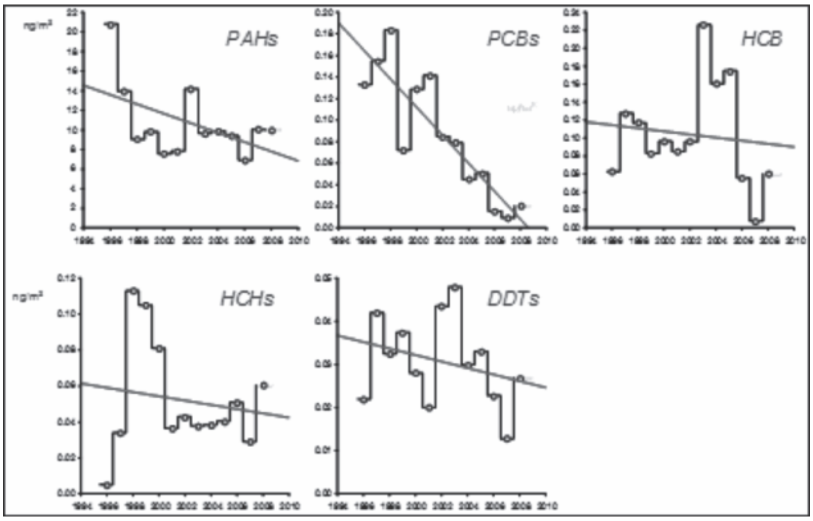

Figure 5. Time-bound trends of the atmospheric levels of POPs in Košetice.

The integrated monitoring programme allows for comparison of the long-term trends of the POP levels in various matrices. Data from Košetice integrated monitoring can be used for an assessment of sources and distribution processes, and for validation of long-range transport and environmental fate models [9,10].

Conclusion

Integrated monitoring at Košetice observatory represents very unique sets of long-term environmental data on the Central European background level. These long-term results of POPs determination in air and other environmental compartments serve as a very useful base for the evaluation of temporal and spatial trends of POPs on a regional scale, a base which can used for model validation, comparative studies, prognosis, scientific projects, for a study of environmental processes.

The observed trends of environmental scale confirm the decreasing trends in the last years in the Central and Eastern Europe, which is in very good agreement with other European sites and sites from other part of the Globe.

Acknowledgements

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BULK ATMOSPHERIC DEPOSITION OF PERSISTENT TOXIC SUBSTANCES (PTS) ALONG ENVIRONMENTAL GRADIENTS IN BRAZIL

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Abstract

Bulk atmospheric deposition for selected Persistent Toxic Substances (PTS) was performed along environment gradients (urban-rural-remote sites) in Brazil. This work is motivated by the lack of knowledge on the fate of PTS and its imitations in South America, particularly along environment transects. Bulk samplers (polyurethane foams 1x1m^2) were fixed over summer and winter periods at urban, rural and mountain sites (2005-2007) comprised different regions of Brazil. Organochlorine pesticides (OCs) and polychlorinated biphenyls (PCBs) were analyzed by gas chromatography with electron capture detection (Shimadzu 2010, 20i CG-ECD). As a result, urban sites reported the highest overall deposition rates for PTS, which ranged from tens to thousands of pictogram per m^2 per day. The results of this study are important in showing that even regulated, selected PTS are still impacted by local and regional emissions in Brazil, probably associated with the historical and continued emissions from old PTS stocks.

Key words: Persistente Toxic Substances (STPs); atmospheric deposition; organochlorine pesticides; PCBs; endosulfan; DDT; environment gradients; Brazil

Introduction

Persistent Toxic Substances (PTS) are environmentally persistent substances that can be found in remote areas far removed from their sources that still display some level of toxicity. Their transport from emission sources are controlled by climate and geographical parameters like precipitation rates, winds and low temperatures[1]. Due to their physical chemical properties, these semi-volatile compounds can be present in the atmosphere gas phase and/or bound particles that are susceptible to atmospheric removal largely driven by deposition mechanisms[2].

According to the South America UNEP PTS regional report, the massive use of PTS in South America is derived mainly from industrial, agricultural and sanitary uses[3]. Historically, Brazil is one of the most South American countries that experienced an extensive use of PTS in the past which may include legacy compounds as PCBs, DDT, lindane and toxaphene[4]. Although there is a still huge knowledge gap on the PTS fate in Brazil, previous studies have pointed out high levels of PTS in many abiotic and biotic environmental matrices[5,6]. Nevertheless, just a few of them are focused on PTS atmospheric studies where it is believed that is the main transport of these semi-volatile compounds in the environment[7,8].

The present work makes a screening of selected PTS atmospheric deposition following environment gradients which were fixed in different parts of Brazil (Northern-Southeast-Southern). Bulk atmospheric deposition systems were performed for selected PTS during 2005-2007 at urban, suburban, rural and remote sites. This work is motivated by the lack of knowledge on the fate of PTS and its imitations in South America, particularly along environmental transects.

Materials and Methods

<u>Deployment:</u> This work included nine monitored sites in Brazil following environmental gradients (urban-suburban-rural-remote sites) in Rio de Janeiro, Santa Catarina and Acre states with sampling conducted during 2005-2007. Remote sites included two high mountain sites that was situated at the National Park of *Serra dos Orgãos* – LAT 22°26'56''S LOG 42°59'05''W – Rio de

Janeiro State and the National Park of *São Joaquim* – LAT 28º00'49''S LOG 49º35'17''W – Santa Catarina State.For each monitored site, two PU foams samplers were deployed following over winter and summer periods for approximately 30 days each. The samples were deployed along environmental gradients and mounted in open areas (1.5-2.0 m above ground) to ensure no obstruction airflow. Field blanks were deployed once during each season for the two National Parks involved (n=4 in total).

Extraction and Analysis: Sample preparation, extraction and clean-up were modified from Pereira et al., 2007. Briefly, the PU foams samples (effective area = 0.36 m^2) were Soxhlet extracted over 20 hours with 250 mL of petroleum ether. The extracts were cleaned using an open column filled with 3 g of deactivated acid silica (10%) topped with 2 g of alumina and 0.5 g sodium sulfate, and then eluted with 25 mL of dichloromethane/methanol mixture (9:1). The cleaned extracts were concentrated by rotary evaporation and nitrogen blow-down to a volume of 500 μL and solvent exchanged to isooctane. Tetrachloro-m-xylene (TCMX) was added as an internal standard (100 ng) for volume correction to all sample extracts prior to analysis. The instrumental analysis of the extracts was carried out by gas chromatography with electron capture detection (Shimadzu 2010, 20i CG-ECD).

Extracts were analyzed for the presence of target compounds that included polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCs). Samples were screened for 28 PCBs: PCBs -8, -18, -28, -31, -44, -52, -66, -77, -81, -101, -105, -114, -118, -123, -126, -128,-138, -153, -156, -167, -169, -170, -180, -187, -189, -195, -206, -209; and 24 OCs: *α*, *β*, *γ* and *δ* –hexachlorocyclohexane (HCHs), hexachlorbenzene (HCB), aldrin, dieldrin, endrin, isodrin, heptachlor, heptachlor epoxide, *cis*-chlordane, *trans*-chlordane, endosulfan I (Endo I), endosulfan II (Endo II), *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT, metoxichlor, mirex. Limits of detection (LOD) in air samples were defined as average of field blanks (n= 4) plus three times the standard deviations.

Results and Discussion

Method recoveries for target PTS were generally > 85%. No recovery correction was applied to the results. In this study, the LOD values ranged from 0.1 ng to 6.5 ng for OCs and 0.03 ng to 6.9 ng for PCBs. The results were reported only if the signals exceeded the baseline noise values thre times. In this study, both laboratory and field blanks were below the LOD values for all target compounds.

As a result, urban sites reported the highest overall deposition rates for PTS, which ranged from tens to thousands of pictogram per m^2 per day (table 1). On the other hand, no clear trends were observed for seasonal variations of PTS deposition rates. Among OCs, DDT and its metabolites were constantly detected in relatively high deposition rate levels (>1000 $pg.m^{-2}.day^{-1}$). Following this, other legacy and current-use pesticides as HCH, dieldrin, aldrin, metoxichlor, chlodanes, HCB and endosulfans were also detected in this study (10-100 pg m^{-2} day^{-1}). High total endosulfans (*alpha* + *beta* isomers) deposition rates were main observed at rural and mountain background sites, which probably indicate the high potential of this current-use insecticide to a long range atmospheric transport (Figure 1).

Table 1 – Range and median concentration for PTS deposition rates (pg/m^2/day^{-1}) along different environment gradients

	Urban	**Suburban**	**Rural**	**Remote**
HCB	77 (7-97)	15 (BDL-26)	7 (BDL-13)	26 (22-30)
Chlordanes	62 (BDL-217)	17 (3-22)	13 (BDL-25)	15 (11-19)
Metoxichlor	138 (BDL-190)	BDL	BDL	BDL
Dieldrin	285 (BDL-355)	BDL	BDL	20 (BDL-40)
Aldrin	16 (BDL-49)	11 (BDL-30)	BDL	29 (20-37)
[illegible]	42 (17-145)	15 (BDL-122)	206 (125-288)	72 (10-133)
ΣHCH	158 (BDL-215)	165 (32-205)	723 (60-86)	223 (83-362)
ΣDDT	2308 (609-3642)	130 (BDL-601)	163 (161-165)	19 (11-27)
ΣPCB	4992 (2410-5520)	2216 (1430-2140)	1785 (1430-2140)	2963 (2900-3025)

*Urban sites – Rio de Janeiro, Santa Catarina and Acre states; Suburban sites – Rio de Janeiro and Santa Catarina States; Rural sites – Santa Catarina States; Remote sites – Rio de Janeiro and Santa Catarina States.

For the sum of PCBs, extremely high deposition rates were also mainly observed at urban sites (>5000 pg m^{-2} day^{-1}) reached basically 2 to 4 times higher compared with overall remote and rural monitored sites (Table 1). In a preview study, Pereira et al.(2007) have also reported a similar deposition trends with extremely high PCB levels close to industrialized and urban areas (Rio de Janeiro State) that reached 6 to 10-folds higher compared to background sites. Historically, Brazil is one of the most PCB consumers where around 6.7% of the total amount of Aroclor was consumed[4]. Although there is a still huge knowledge gap on the PCB fate, for the majority of the South American countries, previous studies have pointed out the presence of different PCB congeners in many abiotic and biotic environmental matrices[5,6]

These results are important in showing that even

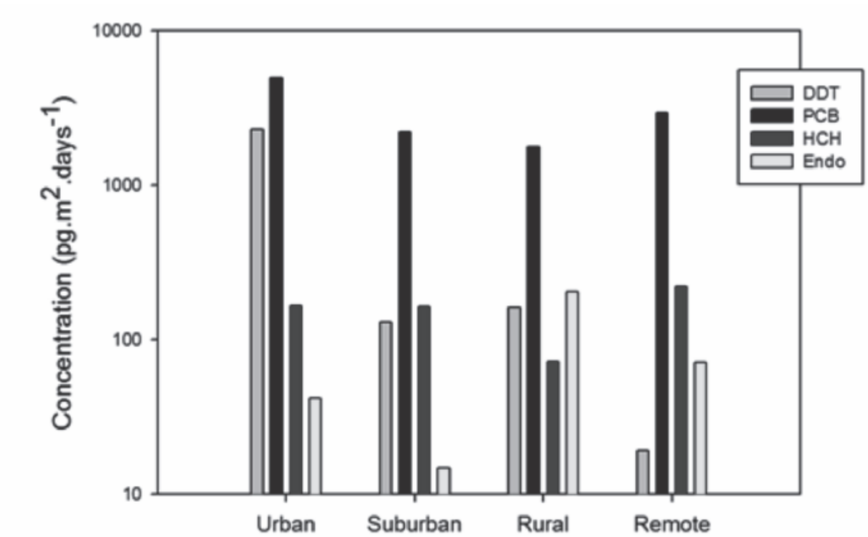

Figure 1. Deposition rate (pg m^2 day^{-1}) concentrations in different environment sites.

regulated, selected PTS are still impacted by local and regional emissions in Brazil, probably associated with the historical and continued emissions from old PTS stocks.

Acknowledgements

This work was partially funded with resources from CNPq – Prosul (014/2006, Brazil). Special thanks to the "Instituto Chico Mendes de Biodiversidade" (ICMBio) that permitted our access at the two National Parks investigated. Dr. Torres is Researcher of CNPq - Level 2, "Jovem Cientista do Nosso Estado" (FAPERJ) and Advance Fellow at the Mount Sinai School of Medicine and is funded by Grant 1D43TW00640.

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CASE STUDY OF OBSOLETE PESTICIDES POLLUTION AROUND THE PESTICIDES LANDFIL FROM THE REPUBLIC OF MOLDOVA

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Abstract

The pesticides landfill located in the southern part of the Republic of Moldova in the Unit Territorial Autonomy Gagauzia area is considered as one of the national priority sites and requires urgent attention in order to eliminate acute risks for public health and environment. Over the period 1977-1987, 3,940 tons of pesticide waste, collected from various locations in the country, were buried there, including 654.1 tons of DDTs. The site is only a few km away from the Ukrainian and Romanian borders and close to watersheds discharging in the Prut River and the Danube near to its estuary. Under the Action Plan for Implementation of Stockholm Convention on Persistent Organic Pollutants, were conducted research studies around the site in the NATO Science for Peace Project "Clean-up chemicals – Moldova" and showed migration at least 10 dangerous pesticides (atrazin, simazine, alpha-HCH, beta-HCH, Gamma-HCH, delta-HCH, dazomet, prometryn, triflualin, DDTs) and sulphur containing compounds characterized in the mass spectra through 6, 7 or 8 sulfur atoms. Thus, it will contribute in solving the most pressing issues related to environmental quality and human health, the integration of environmental concerns in national economy sectors and promotion of sustainable development.

Key-words: obsolete pesticides residues, Science for Peace and Security Programm, inhomogeneous distribution, environmental monitoring

Background

In 1970 a special dump site was built in the southern part of the country, in the proximity of the village Cismichioi that is located in the Unit Territorial Autonomy Gagauzia area of the Republic of Moldova. Over the period 1977 - 1987, 3,940 ton of pesticides waste, collected from various locations in the country, were buried there, including 654.1 ton of DDTs.

The pesticide landfill at the Cismichioi site is considered as one of the national priority sites and requires urgent attention in order to eliminate acute risks for public health and environment. The 2.3 ha site contains 16 distinct burial mounds, most of which are visible from the surface. In only 4 of these sites the wastes were buried in protected conditions, in the others the chemicals are only kept isolated from the surrounding soil with a layer of plastic foil. The site is only a few km away from the Ukrainian and Romanian borders and close to watersheds discharging in the Prut River and the Danube near to its estuary.

Local administrative and environmental officials claim that the occurrence of cancer is abnormally high in the area. In addition, many people report breathing difficulties. Local residents also claim that in warm weather conditions (summer months) fog can be seen rising from the site that moves in the direction of the village of Cismichioi, which is located southeast of the landfill.

Study Areas and Sampling

The particular area of research was selected from a number of other ones on the basis of the large amount of buried pesticides (close to 4,000 ton of pesticides waste) and of the toxicity and persistence of these compounds (POPs and other pesticides). The geographic proximity to Romanian and Ukrainian borders (5-10 km) and to the Lower Danube and Black Sea also played a role in the selection of the site.

Four areas (located to the North, East, Southern and the West outside the landfill) were selected from which samples were collected to obtain information on the environmental status of residues in the selected area. The most important questions to be answered were whether pesticide residues levels in soil could be linked to dispersal from the landfill site and how high could be risk for public health, fauna, flora, etc.

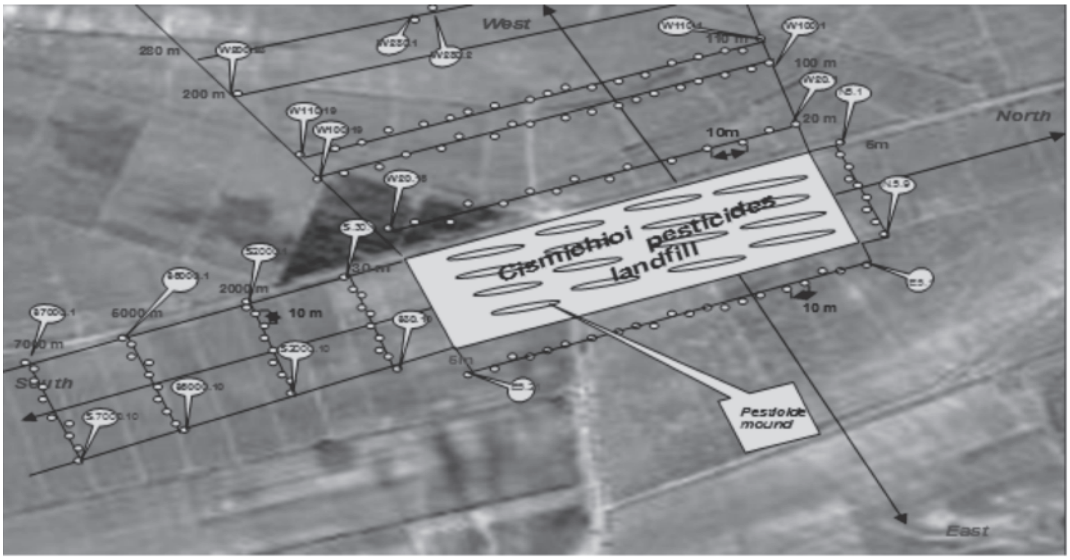

Figure 1. A map of the area which indicates the sampling locations (distance not to scale)

The general strategy for sampling was designed to obtain answers to the following questions:

- to study more prominent pesticides migration at different distance far from landfill parallel with landfill wall;
- to study the variety of pesticide residues content dependent on the sampling period;
- to investigate how pesticides migrate in dependence of depth of sampling.

A total of 216 soil samples were collected in the study areas between February 2009 and August 2009 in different weather conditions: spring (April with wet weather and heavy winds), summer (May to August hot, so usually a dry period with heavy winds but including sampling during June, after rain showers) (Fig 1). On every selected sampling point were collected topsoil (from 0 to 30 cm) and subsoil (from a depth of 90 cm to 100 cm) using a soil auger. The top surface layer with vegetation was always removed. After each sample was collected, the soil auger was rinsed with tap water and dried before the next use.

The results as shown in the tables that follow provide the average of 3 separate analyses. In case one of the analyses provided one result below the detection limit, the average of the two remaining analyses is reported. Most of the samples analyzed were obtained to the South and the West because these are the directions of water flow away from the site.

Chemicals

High purity grade solvents such as hexane, Chromasolv® (Sigma-Aldrich, grade purissimum, assay ≥97.0%) and dichloromethane Chromasolv® (grade purissimum, assay ≥99.8%) were purchased from Sigma Aldrich and were used for GC-MS analysis. Exceptionally technical purity grade reagents of hexane with grade purissimum with assay ≥95% and acetone grade purissimum, assay ≥99% from Fluka were used, which were distilled and evaluated by GC-MS analysis for purity checks prior to their use for analysis.

Pesticide Standards

A number of pure compounds were used as pesticide standards and were obtained from the companies as indicated:

- From Blok-I (НПК «Блок-1»), Russia: atrazine 98.9% (Russian State standard sample-74-90-98), simazine 99.5% (ГСО-75-05-98), DDT 99.0% (Russian State standard sample ГСО-7379-97), gamma-HCH 99.6% (Russian State standard sample 11-34-2005);
- From Ecolon (НПК «Эколон»), Russia: DDE 99.0% (standard sample 01-03), DDD

99.0% (standard sample-02-03) , alpha-HCH 98.6% (standard sample-12-06), beta-HCH 98.7% (standard sample-11-06)
- From Mackteshim Agan, Israel: promertryn 99.5% (7287-19-6).

Sample Extraction

The soil samples were dried at room temperature for 120 h in a separate room from the analytical laboratory. The analysis of each sample was executed in triplicate: each dry soil samples (10 g) was weighed and 20 mL of H_2O was added. To the sample mixture were added 40 mL of acetone and shaken using a shaker (type OS-10, „Biosan", Lituania) for 1h. The extract was filtered through paper filter (type ODS C18 SPE, AccuBond, Agilent). The soil extract was then subject to the clean-up.

Clean-up of soil extracts

After the first extraction 10 mL hexane was added to the soil samples and then extracted again with a mixture of 10 mL water and 30 mL of acetone. After filtration, to the extract collected in an Erlenmayer flask were added 180 mL H_2O and 40 mL hexane, extracted with hexane in duplicate, dried with anhydrous Na_2SO_4 and then evaporated at temperature 40^0C on a rotary evaporator (Heidolph Laborota-4000 G3 Efficient, Germany). The extracts were dissolved in 1 mL acetone. No additional clean-up was needed and the extract was ready for GC-MS analysis[1].

Gas Chromatographic - Mass Spectrometric analysis

Quantitative analysis of the residues of POPs and pesticides in soil was done using a gas chromatograph (GC Agilent Technologies 6890 N) connected with a mass selective detector (MSD, Agilent Technologies 5973) equipped with a SPLITLESS.LO programming. The capillary column used is HP-5MS (30m x 0.25mm x 0.25 µm). Helium with high purity of 99.9999% was used as the carrier gas at 10.48 psi, at a constant flow of 37 cm^3/sec. Samples (10 µL) were injected in the splitless mode with a total flow rate at 7.5 mL/min. The front inlet and detector (MS Quad and MS Source) temperatures were: 275, 150 and 230°C, respectively. The temperature program of the oven was: 100°C (held for 30 seconds), 10°C/min to 180°C, 3°C/min to 250°C, 10°C/min to 290°C and then held at that temperature for 10 min. An example of a typical mass spectrum (DDT) is shown in Figure 2.

The procedure used for GC-MS analysis of pesticides residues in soil was provided by Professor Adrian Covaci (University of Antwerp, Belgium) and Dr. Lourdes Ramos (Consejo Superior de Investigaciones Cientificas, Madrid, Spain).

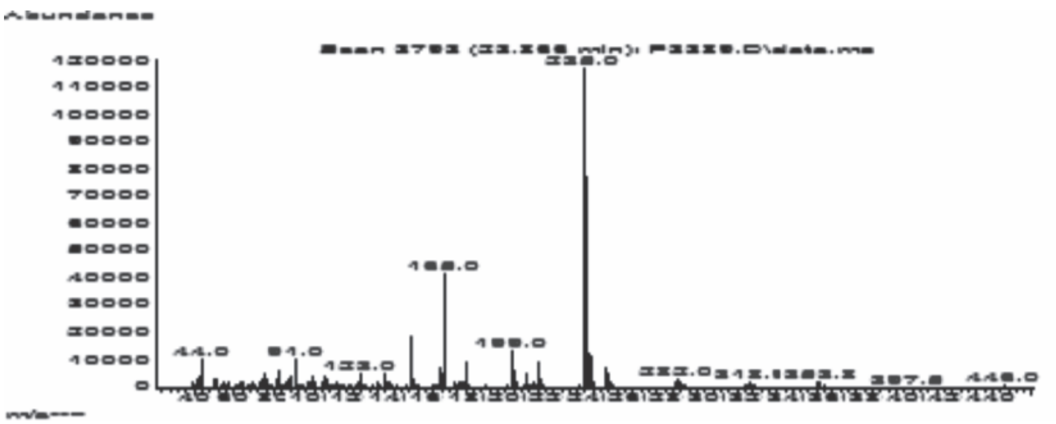

Figure 2. Mass spectrum of DDT showing the target ion (235)

[1] Klissenko, M.A., Alexandrova, L.G. The determination of residual quantities of pesticides (russian), Kiev: Zdorovia, p.174, 1983.

Results

Calibration

Linear calibration curves were found between peak areas and analyte concentration over the whole range studied. Calibration curves were obtained for the quantification using a mixture of standard solutions of chlorinated pesticides dissolved in hexane and mixture standard solutions of simm-triazine pesticides dissolved in acetone at a concentration 1, 5, 10, 25 and 50 μg/mL. Retention time, masses and relative abundance of the confirmation ions to the quantification ion were used as identification criteria.

The content of all pesticides detected in soil samples during this study were presented in mg/kg dry weight and compared with maximum residues level (MRL) for each pesticide. The retention time and MRL for select pesticides are presented in Table 1.

Table 1. Analytical details

Compound	t_R (min)	Fragment ions in GC-MS		MRL RoM (mg/kg soil)	Maximum Allowable Concentration MAC, EU[2] (mg/kg soil)
		Target ion(m/z)	Confirmation ions (m/z)		
Simazine	11.26	200	44,186,173	0.2	0.2
Atrazine	11.41	201	215, 58, 173	0.5	0.2
Prometryn	14.32	241	58, 184, 226	0.5	0.2
DDE	19.94	246	318, 176	0.1	0.1
DDD	22.02	235	165, 199	0.1	0.1
DDT	23.88	235	165, 199	0.1	0.1
alpha-HCH	10.65	181	219, 109, 254	0.1	0.1
beta-HCH	11.56	181	219, 109, 254	0.1	0.1
gamma-HCH	11.64	181	219, 109, 254	0.1	0.1

Pesticide Residues in soil

Between February 1, 2009 and December 31, 2009, 216 soil samples were analyzed by GC-MS and HPLC for the selected more toxic and persistent pesticides in the environment. The analysis of these 216 samples of soils was repeated three times for its quality assurance. Thus 711 soil samples in total were analyzed.

Pesticides were identified in 77 % (167 samples) of the soil samples tested. The pesticides such as simazine, atrazine, prometryne and DDT and its breakdown products (p,p-DDD and, p,p-DDE) summarizes the occurrence of the pesticides detected in study area soils.

Pesticide Residues in soil samples from Northern part of landfill

The study concentrated on the 30-cm surface/top soil layer. Nine samples were taken from the northern part of landfill, at 5 m away from wall of the dump site and with a distance of 10 m between samples. DDTs was the only pesticide detected in soil samples from this area. The DDTs breakdown products (DDE and DDD) were detected in 8 out of 9 samples. DDT was detected in 6 samples. Other pesticides such as α-HCH, β-HCH, γ-HCH, atrazine and prometryne were systematically looked for but never appeared with a concentration above the detection limit.

The results for the sum of DDT and related compounds are summarized in the Figure 3.

Pesticide Residues in soil samples from Eastern part of the landfill.

The study was again concentrated on 30-cm surface/top soil layer. Twenty one samples were taken at a 5-metre distance from the wall of the dump compound and with a distance 10 m between each sample (Fig 1). Six pesticides were detected in soil samples from this area.

Compounds such as α-HCH, β-HCH, γ-HCH were systematically looked for but not detected. All pesticides detected in these samples were <MRL except for simazine in one sample (at 0.23 mg/kg). We point to the following observations:

[2] Soil Quality. TCVN 5941 – 1995.

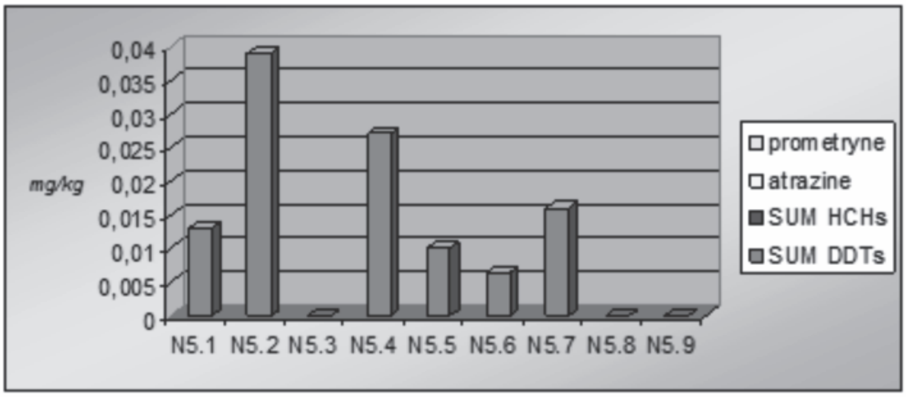

Figure 3. Pesticide Residues in soil samples from Northern part of landfill

1. DDT and its breakdown products (DDE and DDD) were detected <MRL (0.1 mg/kg) in all the samples. The maximum concentration encountered was 0.057 mg/kg).
2. Atrazine was detected in 5 soil samples with maximum concentration (0.033 mg/kg) i.e. well below the MRL of 0.5 mg/kg. Prometryne was detected in 4 samples with maximum concentration of 0.083 mg/kg again < MRL. Simazine was detected in 6 samples; one concentration exceeded the MRL value at 0.23 mg/kg. HCHs products were not detected (Fig 4).

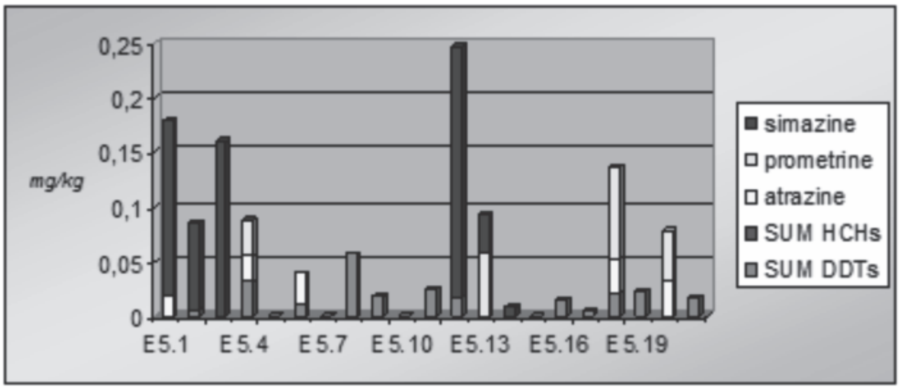

Figure 4. Pesticide Residues in soil samples from Eastern part of the landfill

Pesticide Residues in soil samples from Southern part of landfill

Forty samples were taken 50-cm surface/top soil layer at distances ranging from 30 m, 2000 m, 5000 m and 7000 m away from the landfill site wall. This direction slopes into a hill.

Prometryne was not detected in any of the samples. The DDT compounds and atrazine were always <MRL. Results are as follows (see Figure 5 a, b, c, d). DDT was detected below the quantification limit (0.1 mg/kg) in 3 samples out of 10 at 30 m with a maximum concentration of 0.006 mg/kg. At 2000 m it was detected in 7 samples out of 10 samples with a maximum concentration of 0.015 mg/kg while at 5000 m one sample showed DDT with a maximum concentration of 0.011 mg/kg. At 7000 m 10 samples DDT and DDE were detected with a maximum concentration in one sample of 0.034 mg/kg. Atrazine was detected below the quantification limit (0.5 mg/kg) at 5000 m in 3 soil samples with a maximum concentration (0.022 mg/kg) and at 7000 m, in 8 samples with a maximum concentration 0.41 mg/kg. HCHs pesticides were detected in 3 soil samples at 5000 m and 7000 m each with a maximum concentration 0.35 mg/kg above the MRL (0.1 mg/kg).

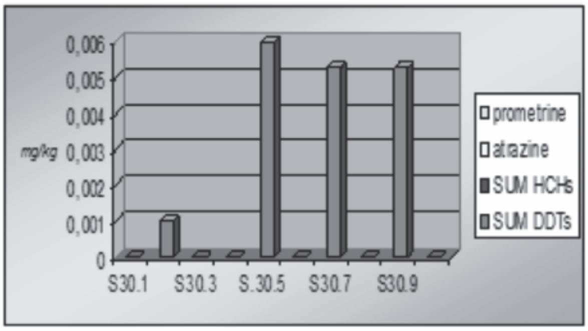

Figure 5a. Content of pesticides residues detected in soil samples at 30 m away from the landfill.

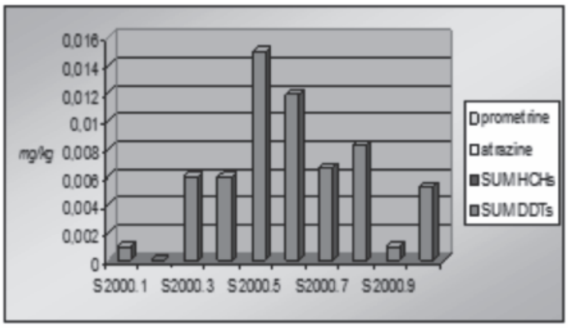

Figure 5b. Content of pesticides residues detected in soil samples at 2000 m away from the landfill.

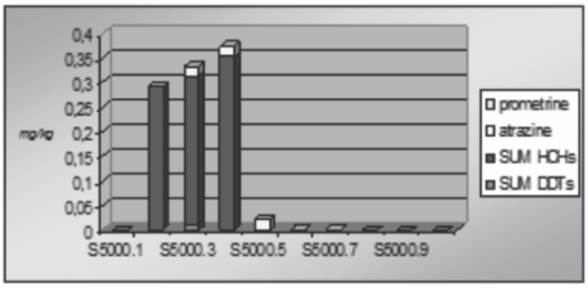

Figure 5c. Content of pesticides residues detected in soil samples at 5000 m away from the landfill.

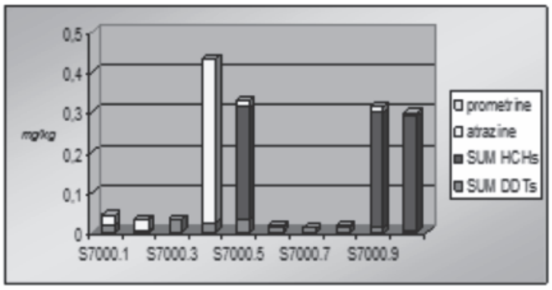

Figure 5d. Content of pesticides residues detected in soil samples at 7000 m away from the landfill.

Pesticide Residues in soil samples from Western part of landfill

Table XIII summarizes the results for a total of 145 samples were taken at different distances from the dump site (20, 100, 110 and 200 m) in different sampling periods (29 April 2009, 27 May 2009, 26 June 2009 and 13 August 2009). Samples were taken from the 50 cm surface/top soil layer and at 1 m depth.

The results show that DDTs products were detected below the MRL in a number of samples at all distances with a maximum concentration of 0.016 mg/kg at 20 m and a maximum concentration of 0.268 mg/kg at 100 m above the MRL at 0.1 mg/kg. HCHs products were detected only in one samples at 100 m (0.09 mg/kg) and two positive measurements at 280 m (0.02 mg/kg). Simazine, atrazine and prometryne were occasionally, but not systematically, detected at concentrations exceeding occasionally the MRL values.

Discussion

The results obtained show that the concentration levels of the pesticides overall do not exceed the safety limits. Up to the present time, the site does not seem to discharge pesticides in the environment. MRL or MAC values are only exceeded in a few of the samples analyzed.

With the information available in the literature it is possible to compare the results obtained with other data obtained elsewhere. One basis of comparison is soil from a rural area near Iassy, Romania where DDT levels are 0.228 $\pm$ 157 mg/kg[3]. In other Romanian locations concentration levels of 0.0625 $\pm$ 0.044, 0.303 $\pm$ 0.087 and 1.05 $\pm$ 0.69 (near Timisoara, Arad, Ploiesti, Cernavoda) are reported. Another study reports concentration of organochlorine compounds in the following range: 0.2–1.4, 5–56, and 5–95 ng/g of soil for HCB, sum HCHs, and sum DDTs, respectively[4]. Overall, the results obtained do not show abnormal levels of pollution with the compounds that could point to leakage of the pollutants from the storage site.

[3] Covaci A., Hura C. Schepens P., The Science of the Total Environment 280 (2001) 143-152

The results show a quite inhomogeneous distribution of the concentration levels. Hence, it is not possible to see any systematic trends as a function of distance or depth. Figures 5 ***a-d*** and Figure 6 ***SUM DDTs*** (a) and ***Simazine*** (b) illustrates this for measurements to the South of the landfill.

Figure compares the concentration of the sum of the DDT products at the surface and that at a depth of 1 m on the west of the landfill with the surface concentration being systematically higher than that in depth. A similar observation can be made for simazine.

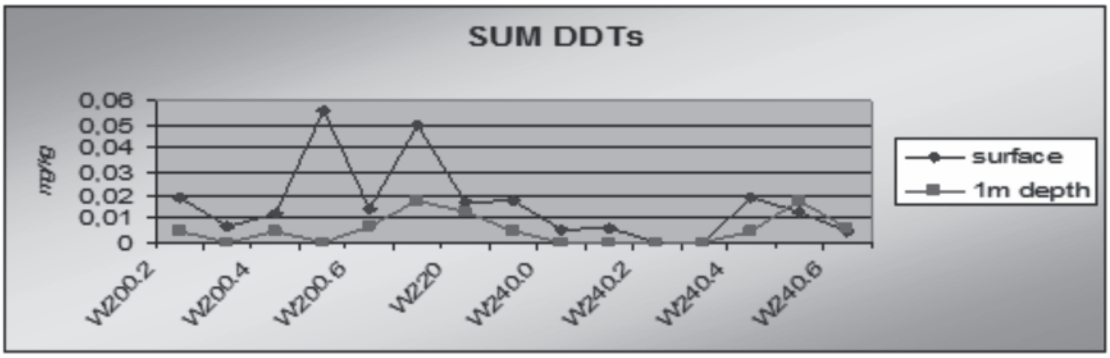

Figure 6a. Comparison of surface and depth concentration of DDT at depth 1 meter for locations at 200 m to the west of the landfill

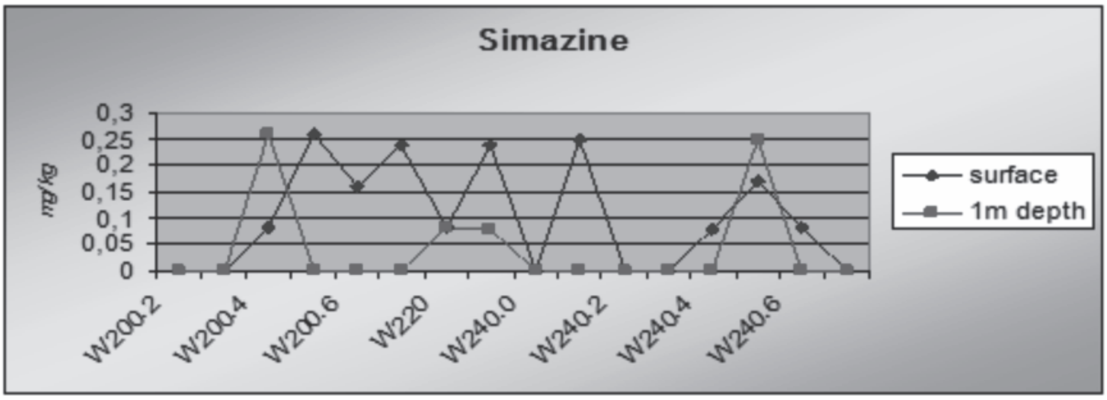

Figure 6a. Comparison of surface and depth concentration of simazine at depth 1 meter for locations at 200 m to the west of the landfill

Conclusion

It appears from this limited study that until now there is no dramatic increase in pesticide levels around the Cismichioi landfill. However, illegal use, package deterioration, or accidents may cause localized or widespread pollution at this and other sites, thus representing a potential risk to human health and the environment. Hence, further studies in this area are needed in order to assess the levels of pesticides until the site is remediated.

[3] Dragan D., Cucu-Man S., Dirtu A.C., Mocanu R., Van Vaeck L., Covaci A., Intern. J. Environ. Anal. Chem. Vol. 86, No. 11 (2006) 833–842

PERSISTENT ORGANIC POLLUTANTS IN THE FRAMEWORK OF MONITORING OF AGRICULTURAL SOILS IN THE CZECH REPUBLIC

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Abstract

Persistent organic pollutants (POPs) are represented by a group of substances, which are very stable in the environment and can be transported for a long distance. They are accumulated in all animals, including humans and can cause many health problems. In order to prevent further spread of these compounds the Stockholm Convention on Persistent Organic Pollutants was created. The Czech Republic signed and ratified the Convention in 2002. Seven substances from the Convention (7 PCB congeners, HCB, 4 HCH isomers and DDT and its metabolites) are monitored by the Central Institute for Supervising and Testing in Agriculture (ÚKZÚZ). POPs have been observed by ÚKZÚZ since 1994 at 40 monitoring plots. These plots are a part of so called Basal Soil Monitoring System (BSM), which has been in operation since 1992 and consist of 214 monitoring plots. Soil samples are collected every year from topsoil and subsoil layers. In order to get the information about possible transmission of POPs from soil to plant, the system was enlarged to monitoring of POPs content in plants. For this purpose 12 monitoring plots with elevated POPs contents in soil were selected for plant sampling.

Long-term soil monitoring gave us information about POPs content and its changes in agricultural soils. POPs contents are stable during the years with the exception of PCBs. Contents in topsoil are higher than in subsoil. POPs contents in plant samples are below the limit of quantification except for two samples – rape and clove-grass mixture. It seems to be obvious that POPs contents in plant is not solely dependent on POPs content in soil but that the uptake is influenced by the type of plant and other environmental conditions.

Key words: persistent organic pollutants (POPs), soil, plant, monitoring

Introduction

Persistent organic pollutants (POPs) are substances which persist for a long time in the environment. They have some typical characteristics – high tendency to bioaccumulation in fatty tissues of humans and wildlife, high level of chemical and biological stability and by an ability of long-distance transport. Due to these characteristics, they are able to disperse thousands of kilometres from the source and to contaminate the whole biosphere. It is generally known that the cyclic evaporation from soil and water surface which causes air drifting of POPs in the form of vapour and dust and subsequent rain, snow or solid particles deposition is the mechanism explaining the POPs mobility in the environment.

Persistent organic pollutants are created by processes in nature (e.g. volcanic activities, fires), however, the overwhelming part of their sources is of anthropogenic origin. Observing of the beginning of the food chain – soil quality – is one of the ÚKZÚZ tasks. For this purpose the Central Institute for Supervising and Testing in Agriculture monitors the contents of selected POPs (7 PCB congeners, HCB, 4 HCH isomers (a-, b-, g-, d-) and DDT and its metabolites) in agricultural soils and plants.

Material and methods

Soils

Soil samples were taken within Basal Soil Monitoring System (BSM). The system was established in 1992, when also the first samples were taken in basal net (basal soil monitoring subsystem) of 190 monitoring plots. Five years later, in 1997, there was established the subsystem of contaminated plots. In total 27 monitoring plots were created on the sites characterised by inorganic contamination of both anthropogenic and geogenic origin.

Monitoring plots are defined as rectangles measuring 25m x 40m (1000m^2). Each plot is characterised by geographical coordinates, landscape morphology and climatic and soil conditions. There are three sampling schemes in the frame of monitoring.

Fig. 1 Parameters determined in the samples within individual sampling schemes

Initial sampling	**Basic sampling (six-year period)**	**Annual sampling**
• Actual moisture, reduced bulk density, porosity, maximum capillarity, actual air capacity, texture • C_{ox}, N_{tot}, CEC • Hazardous elements in Aqua Regia (As,Be,Cd, Co,Cr,Cu,Mo,Ni,Pb,V,Zn; Hg_{tot}) • Soil pit description • Identification of the monitoring plot	• pH – H_2O, $CaCl_2$ • Available nutrients and micronutrients (P,K, Mg,Ca in Mehlich III; B,Mo,Mn,Zn,Cu) • Hazardous elements in Aqua Regia and 2M HNO_3 (As,Be,Cd,Co, Cr,Cu,Mo,Ni,Pb,V, Zn; Hg_{tot}) • C_{ox}, N_{tot}, CEC	• N_{min} • Microbiological and biochemical parameters • Organic pollutants - HCH, HCB, DDT and its metabolites, PCB, PAH • Hazardous elements content (+ POPs) in agricultural plants • Evidence of fertilization and pesticides application On selected plots only!

As mentioned in Fig. 1, POPs are analysed in samples taken annually. The samples of arable soils are taken from topsoil (according to the thickness of the horizon, maximally to 30 cm) and from subsoil (30–60 cm), within hop gardens from topsoil (10–40 cm) and subsoil (40–70 cm); within permanent grassland from three horizons (0–10 cm, 11–25 cm, 26–40 cm; always after the removal of top turfy layer). Samples for POPs analysis are taken by zig–zag pattern. Sampling for this purpose was started in 1994. At first samples from plots, on which wheat was planted, were taken (alterative set of plots). In 1997 a stable/fix set of 40 plots in BSM system and 5 plots in protected areas were set in. ÚKZÚZ samplers are responsible for good-quality sampling. Polychlorinated biphenyls (PCB) have been determined since 1994: in 1994–1997 3 congeners were determined (138, 153 and 180), other 3 congeners were added in 1998 (28, 52 and 101) and 7 indicator congeners have been determined since 2002. Analysis of organochlorine pesticides (OCP) – hexachlorocyclohexane (HCH), hexachlorobenzene (HCB) and DDT and its metabolites have been run since 1994, too, with short break/interruption in 1998 and 1999.

From 2000 PCB analyses and later on also OCP were performed exclusively in ÚKZÚZ laboratory in Brno. In 2004 this test/method was accredited and the compatibility of results was ensured as well. From this point of view only data collected after 2004 (including) were statistically processed in MS Excel 2003, NCSS 2001, Statistica v 6.0.

Plants

With regard to the big environmental importance of POPs our BSM programme was enlarged to monitoring POPs contents in plants. Based on the highest contents of POPs in BSM soils 12 monitoring plots were chosen as suitable for plants sampling. This sampling was started in 2010. Sampling scheme for plants is the same as for soils.

One composite plant sample consisted of at least 10 increment samples and was taken from each monitoring plot (only edible part of plant or plant for feeding). Above–ground part of plant was not washed off. Samples, ranging from 500g to 2000g, were weighed, packed in plastic bags, labelled and immediately transported in a cooling mobile box to the laboratory.

In case of seeds sampling (cereals, rape, poppy) samples were exsiccates, seeds were beaten out, and then weighed. These samples were not cooled down.

Results and discussion

Soils

Every year 90 soil samples are collected and analysed. The contents of HCH in BSM soils are mostly negligible. Majority of the samples do not exceed limit of quantification (LOQ = 0.5 ppb). The LOQ is usually exceeded only in samples from 10 monitoring plots. The maximal value (12.5 ppb) was determined on hop-garden in 2010. Statistical differences between years or horizons were not found. Based on BSM data it would be easy to think of HCH contents in Czech agricultural soils as irrelevant. But lindan (g-isomer of HCH) was a widely used pesticide and generalization of the statement mentioned above is possible only towards larger areas. For example, HCH contents determined in organomineral horizon A were many times higher on the areas of South and Western Bohemia (Čermák et al., 2008) - in arable soils up to 15.4 ppb, in grassland up to 21.1 ppb and in forest soils up to 59.0 ppb and differences between cultures were statistically significant there.

The contents of HCB ranged from < 0.5 ppb to 52.1 ppb. The maximal values were detected on south-eastern and western parts of the Czech Republic. These locations correspond to locations contaminated by DDT substances. There is evidence that HCB was found as an impurity in chlorine pesticides (Škrbić et Durišić-Mladenović, 2007). The HCB contents in topsoil and subsoil differ significantly.

The contents of sum of DDT (DDT_{total} = o´,p´- + p´,p´- isomers of DDT + DDE + DDD) in BSM soils are relatively low. As in the case of HCH when evaluating the locality-burden local conditions must be taken into account (e.g. old contamination, historical application of pesticides). For example the above-mentioned area of South and Western Bohemia (Čermák et al., 2008) is characterised by higher median of DDT_{total} in organomineral horizon A of arable land (42.7 ppb) than BSM soils (and maximal values totalled 879 ppb). The ratio between individual substances of DDT (DDD, DDE, DDT) rises in sequence DDD < DDE < DDT. The contents of DDT_{total} in topsoil are higher than in subsoil (with the exception of grassland). These differences are significant. The contents of DDT_{total} are stable and do not vary significantly through the years.

The contents of PCB (sum of 7 indicator congeners) ranged from 1.75 to 98.8 ppb and varied through the years, but not through the cultures. The PCB contents in topsoil are higher than in subsoil. Quite remarkable locality is Studniční hora (KRNAP – The Krkonoše Mountains National Park). Thanks to its altitude it has a relevant proportion/ratio of the high medians (and averages) in soils originated from protected areas and confirms the big importance of long-range transport of PCB.

The key for selection of monitoring plots designed for plant sampling was that minimally one parameter must exceed limit of particular POP content in soil.

Plants

As mentioned above, 12 plant samples designed for POPs determination were first collected in 2010. The contents of POPs are under limit of quantification (LOQ = 0.05 ppb) almost in all samples with the exception of two samples - rape seed and clover-grass mixture (tab. 3).

In case of rape seed the contents of 3 PCB congeners, g-HCH and 3 DDT substances exceeded LOQ. In case of clover-grass mixture only p´,p´-DDE is above LOQ. All these values are very low.

Also from the point of view of existing legislation, the determined POPs contents in plant samples are low and safe and do not pose any risk for feed/food chain or human health.

From our data it is clear that POPs content in plant does not only strictly depend on POPs content in soil, but also on the type/genus of plants.

Conclusions

BSM data give important information about POPs content in agricultural soils in the Czech Republic. Within more than 10 years of observing stable contents of organochlorine pesticides in BSM soils were statistically approved. In contrast to these substances PCB contents in soils are fluctuating during the years.

Higher contents in topsoil than in subsoil were approved for OCP as well as for PCB. Localities with increased HCB contamination correspond with localities with increased DDT level of contamination.

Plant samples collected on BSM plots contained very low amounts of POPs (POPs contents in the majority of samples were below the limit of quantification). Based on BSM data it is clear that POPs contents in plants do not depend on POPs content in soils. This conclusion will have to be confirmed statistically. Data from BSM are used as a background for specific studies such as possible soil contamination due to floods or fires of industrial buildings etc.

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APPLICATION OF SEMIPERMEABLE MEMBRANE DEVICE FOR ASSESSMENT OF NON-POLAR ORGANICS IN SURFACE AND UNDERGROUND WATER

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The City Jaworzno belongs to the largest towns in Poland. Its area is 152.7 km^2 with more than 96 000 inhabitants. Its biggest environmental problem is related to the contaminated area in the valley of Wawolnica Brook as a result of a chemical plant's recent activities from 1928. Since then plant protection products have been produced, preparation for hygiene and other chemical products has been carried out. To eighties of the twentieth century, the valley of Wawolnica brook was the site of hazardous waste collection from this production.

Release of non-polar organics from industrial activities was assessed by Semipermeable Membrane Device (SPMDs) tool, as a techniques commonly used in various environmental applications for water monitoring. A standard SPMDs were used, delivered as a standard sampling system from a vendor, with its own production of QA/QC. Within two deployments, assessment of non-polar organics was performed. Evaluation of ambient concentration was realized using PRCs approach, as published recently. Using of SPMDs was applied in accordance with ISO 17025 standard. Further evaluation of data sets by marginal and multivariate data analysis supported interpretation of main sources identification.

This work was realised under FOKS (Focus on Key Sources of Environmental Risks) project, with co-funding by ERDF (Central Europe).

Key words: Passive sampling, POPs, OCPs, robust data analysis

POP PESTICIDES IN AMBIENT AIR FROM MONET NETWORK – LEVELS AND TRENDS

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Abstract

The effectiveness of the Stockholm Convention (SC) on Persistent Organic Pollutants (POPs) shall according to Article 16 be evaluated four years after the date of its entry into force. Global Monitoring Plan (GMP) has been developed with an objective of evaluating whether the POPs actually were reduced or eliminated on the global scale. As one of the key matrices for the global monitoring, an ambient air was selected. Two approaches of sampling exist – active using the high volume samplers and passive air samplers (PAS) as new tools for the air quality monitoring.

MONET programme (MONnitoring NETwork) is driven by RECETOX as the Regional Centre of the Stockholm Convention for the region of Central and Eastern Europe on the national scale (MONET-CZ, containing 37 sites including 15 backgrounds), and regional scales – the Central, Southern and Eastern Europe and Central Asia (MONET-CEECs), the Pacific Islands (MONET-PIs), the African continent (MONET-AFRICA) and newly whole Europe (MONET-Europe). The samples are collected in 28-days and they represent 13 samples from each site every year.

Key words|:
Stockholm Convention, MONET, persistent organic pollutants (POPs), ambient air monitoring

Introduction – The Stockholm Convention on POPs and their effectiveness evaluation

The **Stockholm Convention on Persistent Organic Pollutants** (POPs) [1] entered into force on May 17, 2004, and has currently 173 signatory parties (May 16, 2011). The main objective of the Stockholm Convention (SC) is to protect human health and environment from persistent organic pollutants by reducing or eliminating their releases into the environment.

According to Article 16 of the Convention, its effectiveness shall be evaluated four years after the date of its entry into force, and periodically thereafter every 6 years [1]. The objectives of the POPs Global Monitoring Plan are to evaluate whether the POPs actually were reduced or eliminated as requested in Articles 3 and 5 of the Convention. The information on environmental background levels of the chemicals listed in the annexes is a precondition for monitoring of trends over time [1]. In order to meet the objectives of the Global Monitoring Plan (support the preparation of regional reports of comparable information on environmental background levels), the guidance must be provided on how the information is to be collected, analyzed, statistically treated, and reported [2].

Polyurethane foam based passive samplers for sampling of POPs in ambient air

As the air pollution became an issue of great public health concern and the international conventions and new regulations introduced their demands, a pressing need to obtain more air pollutants including POPs data in a cost-effective way appeared. Global Monitoring Plan has been prepared for the purpose of the Stockholm Convention with the objective of establishing baseline trends at global background sites [2]. It was the main goal of the first step of this Global monitoring programme – the determination of basic global information in 2009. When developed parties are to conduct source inventories, identify ongoing sources, and provide environmental monitoring evidence that ambient levels of POPs are declining [2,3].Developing countries in particular require cost-effective and simple approaches. The experiences from the first report in 2009 and the list of newly adopted POPs, will be used for the second assessment in 2015.

Based on the long-term work of many international experts, the Guidance for the Global Monitoring Plan [2], was prepared. As one of the key matrices, the ambient air was selected. We have two basic principles for the sampling of ambient air for POPs determination – a passive sampling and an active one, consisting of high volume air samplers. Since the high volume air samplers as expensive devices requiring reliable power supply as well as trained operators are not widely available, the air monitoring of POPs has only been conducted a limited number of sites. This was also one of the reasons, why a lot of various new types of passive air samplers (PAS) as new tools for the air quality monitoring were introduced in the last years [3-6]. PAS represent a cheap and versatile alternative to the conventional high volume air sampling and they have been currently recommended as one of the methods suitable for the purpose of new long-term monitoring projects. They are capable of being deployed in many locations at the same time, which offers a new option for the large scale monitoring. As it provides information about long-term contamination of selected site, passive air sampling can be used as a screening method for semi-quantitative comparison of different sites with the advantage of low sensitivity to accidental short-time changes in concentration of pollutants.

It was demonstrated that passive air samplers using polyurethane foam (PUF) filters are suitable to study vapour-phase air concentrations of POPs, particularly of more volatile compounds [7-10]. They were successfully applied as a tool for POPs monitoring on the global, regional, national levels and also at a local scale, where they are able to provide site- and source-specific fingerprints. Further they can be used to conduct screening surveys to help to identify the sources [9,10]. This tool based on experiences and results from the long term testing and broad applications was recognized as very useful and effective for the determination of temporal, seasonal and spatial trends on the global, regional and local scales [11].

RECETOX pilot studies

Passive air samplers of this design were first introduced in the Czech Republic in 2002 during the European screening campaign performed by Lancaster University and focused on the atmospheric levels of POPs [7,12]. Since 2003, this research topic has been developed in the RECETOX in cooperation with Lancaster University and Environment Canada.

RECETOX conceptual approach and contribution to wide application of this method was oriented to the long-term study of effects of environmental variables to applicability of this technique for the long-term monitoring and determination of temporal, seasonal and spatial trends on the global, regional and local scales. Samplers were calibrated against the high volume samplers in the field conditions, and their sensitivity, capacity, robustness, as well as an influence of the various meteorological parameters on their performance were assessed [13]. PAS have been continuously deployed in the regular atmospheric monitoring of POPs in Košetice station since 2003 side by side with active samplers to compare information derived from both techniques.

A core network of the Czech Republic was significantly altered based on the evaluation of the results from the pilot study in 2005. The new design was introduced and initiated in January, 2006. Thirteen 28-days samples are collected from each of 37 sampling sites [14,15]. This sampling period and frequency was/is used in main part of MONET sampling sites and campaigns. This monitoring network – MONET-CZ is still flexible and allows further improvements. At the same time, the backbone of the network allows performance and advanced interpretation of the short term spin-off case studies.

The feasibility of the long-term application of passive air samplers for the evaluation of persisting influence of the war damages on the atmospheric contamination of the Western Balkan region was assessed in this study. Results of this project were compared to those of the previous high volume sampling campaigns (APOPSBAL Project) [16,17]. As Central, Southern and Eastern Europe is the region with a lack of data on the atmospheric POP, three screening campaigns were organized between 2006 and 2008 (MONET-CEECs). Sampling sites for the first phase of the MONET-CEECs Project, have been selected in cooperation with the local partners in all participating countries [18,19]. The philosophy was the same as for the model network in the Czech Republic: 5-20 sampling sites were selected per country (according to the size of each country) and they were monitored for 5 months.

In addition to the Central and Eastern European region (CEEC), 26 sites from the African continent (MONET-AFRICA) and 21 sites from the Central Asia (former Soviet Union countries as a part of MONET-CEECs) were monitored in 2008 and 3 sites from the Pacific Islands between 2006 and 2007 (MONET-PIs). MONET-AFRICA now continues by the second phase (2010-2012) [20-22].

Previous **RECETOX studies** [10,11] confirmed that PAS are sensitive enough to mirror even small-scale differences, which makes them capable of monitoring of spatial, seasonal and temporal variations. Passive samplers can be used for point sources evaluation in the scale of several square kilometres or even less - from the local plants to diffusive emissions from transportations or household incinerators - as well as for evaluation of diffusive emissions from secondary sources. While not being sensitive for short time accidental releases, passive air samplers are suitable for measurements of long-term average concentrations at various levels.

Methods - sampler, sampling and analysis

Passive air sampling device used in the pilot studies and MONET programme, methods and sample preparation, analysis including QA/QC procedure are describe in the RECETOX papers and reports [9-11,14,15].

Results

As Central, Southern and Eastern Europe is the region with a lack of data on the atmospheric POP, three screening campaigns were organized between 2006 and 2008 (MONET-CEECs). In addition to the Central and Eastern European region (CEEC), 26 sites from the African continent (MONET-AFRICA) and 21 sites from the Central Asia (former Soviet Union countries as a part of MONET-CEECs) were monitored in 2008 and 3 sites from the Pacific Islands between 2006 and 2007 (MONET-PIs).

Concerning to OCPs, the levels of HCHs were generally low (median value below 30 ng filter^{-1}) except for the sites where it was produced or stored. The highest median levels were measured at several sites in Romania (Turda 2.3 µg, Onesti 1 µg filter^{-1}), similar extreme (2.5 µg filter^{-1}) was also found at Kitengela site in Kenya. Hundreds of nanograms of HCHs per filter were measured in Ufa and Chapaevsk in Russia, near the Spolana chemical factory in the Czech Republic or in Skopje, Macedonia. There were countries as Kyrgyzstan or Romania where all the sampling sites had elevated PCB levels.

Median levels of DDTs stayed below 100 ng per filter at most of the sites. There were, however, the sites with medians higher than the order of magnitude. The highest median level was found at Kitengela site in Kenya (2.5 µg filter^{-1}), the values higher than 100 ng filter^{-1} were also found in Dakar (Senegal) (360 ng filter^{-1}), Asela (Ethiopia), Bamako (Mali), Kyiv (Ukraine), several sites in Bucuresti (Romania) or Kyrgyzstan.

Median values of hexachlorobenzene (HCB) were below 10 ng filter^{-1} at most of the sites. Concentrations several times higher were found in Ivansedlo (Bosnia), Ufa and Chapaevsk in Russia, Kyiv (Ukraine) and Cairo (Egypt). The highest median level was measured in the vicinity of the chemical factory Spolana in the Czech Republic (88 ng filter^{-1}), and near the chemical complex in Chapaevsk. The sites with the highest median levels of pentachlorobenzene (PeCB) as a degradation product of HCB coincided with those with the highest levels of HCB (Spolana, Chapaevsk) but elevated concentrations were also found at all sites of Kyrgyzstan, in Asela (Ethiopia), Kitengela and Dandora (Kenya).

For the purpose of the Global monitoring, however, only the background sites are of interest. To give an overall comparison of the background POP levels in all investigated countries, only the background sites were selected from the database based on available information and measured levels. Each country was represented by one background site. The background site in Kyrgyzstan had the highest median levels of HCHs, followed by the sites in Togo, Tunisia, Romania, Moldova, Ukraine and Serbia. As the background levels of HCHs are usually quite uniform, such results indicate some local sources of HCHs. South Africa and Fiji were found to be the cleanest sites in the project.

As expected, the highest levels of DDTs were determined in Central Africa, especially in Ethiopia and Sudan. High concentration, however, we also found in the South-Eastern Europe (Moldova and Romania). Zambia, Mali and Ghana were elevated, too.

In contrast, Central Europe had the concentration of HCB several times higher than other regions. Even though HCB distributes very well over the large areas, we can still observe high concentration in Central Europe (Czech Republic) and Central Asia (Kyrgyzstan) when compared to the other regions (as Africa). Situation is not so clear for PeCB as a degradation product of HCB. The only site with significantly higher levels of PeCB was in Kyrgyzstan.

Future of MONET

In case of the CEEC, it has been recognized that knowledge on Western European POP levels would greatly improve the understanding to CEEC data. It was the first step and based on this, the harmonization of the monitoring activities in both parts of Europe is a logic step to gain systematic information on the levels and trends of the atmospheric pollution in this continent.

Using mainly the EMEP stations participating in the previous MONET activities and new ones from the rest of European countries and based on the agreement between RECETOX and EMEP, the MONET-Europe, was established in 2009. The goal is to maintain sustainable PAS monitoring at the majority of sites. That would significantly improve the understanding of the sources, fate and transport of POPs in Europe and provide rich information for the modelling databases. At the same time, it would create necessary synergies between the Stockholm Convention and Convention on Long-Range Transboundary Air Pollution (See Fig. 1).

In 2009, the Conference of the Parties of the SC decided that levels of POPs in core matrices will be assessed every six years assuming that such a period will be sufficient for establishment of the temporal trends. As the Košetice station is the only site worldwide where active and passive samplers have been co-employed for full six years so far, results from this station have an important role in the intercalibration of both techniques, comparison of trends derived from both datasets, and development of future global monitoring programmes [16-18]. Long-term

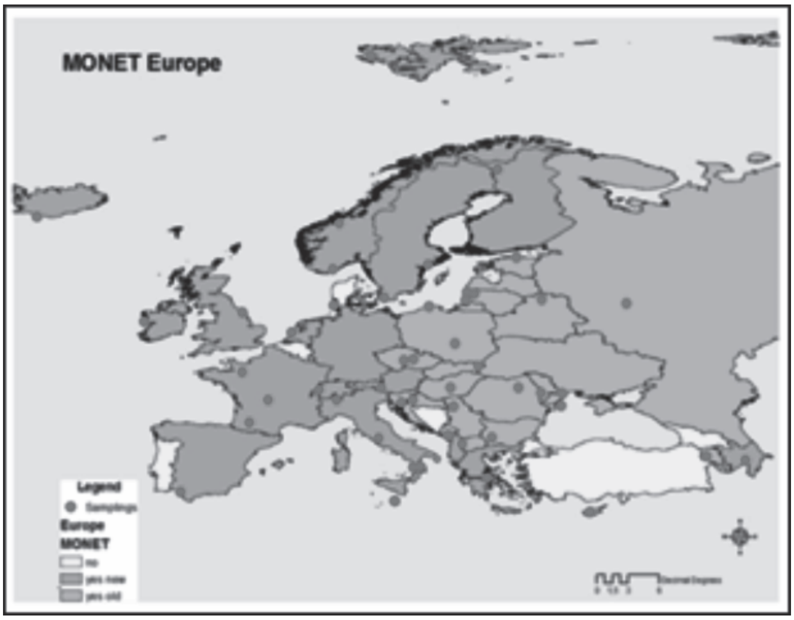

Figure 1. European passive air monitoring network.

sustainability of such monitoring programmes is of a great importance for a success of the Global monitoring plan (Fig. 2).

Figure 2. Global distribution of the sampling sites with on-going air monitoring. MONET sampling sites are coloured blue.

Conclusion

For many of the participating countries the data from MONET programme are the first data on the atmospheric levels of POPs [16-23]. This was the reason why the background monitoring was accompanied with the screening of the extent of contamination in the individual countries. To carry these activities beyond the point of the first screening, best candidates for the background monitoring have to be selected in every region, and resources have to be sought to make the program sustainable.

Now, the harmonization of the monitoring activities in both parts of Europe to gain systematic information on the levels and trends of the atmospheric pollution over this continent, has been started in 2009. The EMEP stations in whole Europe participate in this now MONET phase which is focused on the improvement of the understanding to the sources, fate and transport of POPs in Europe and the providing rich information for the modeling databases.

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MONITORING OF RESIDUES OF PERSISTENT ORGANOCHLORINE PESTICIDES IN SOILS OF UZBEKISTAN

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Abstract

Large amount of pesticides were used in agriculture of Uzbekistan in the past. At present, toxic and persistent pesticides are prohibited to use in Uzbekistan. Persistent pesticides such as DDT and HCHs can be preserved in soil for a long time and can be a source of surface- and ground water contamination. Therefore, monitoring of these pesticides in soils of agricultural areas is one of the tasks of state monitoring program of Uzbekistan. In this paper the results of pesticides monitoring in soils of agricultural areas in Uzbekistan during 2005-2010 are presented. Results show the decreasimg trend of pesticides concentrations in soil of Uzbekistan. For the period of observations, HCH isomers, DDT and its metabolites were determined in soil mostly in amounts less than their maximal admissible concentrations.

Key words: Organochlorine pesticides, residue, soil, contamination, monitoring

Introduction

Modern agricultural production depends on the use of pesticides. Pesticides used to control plants, fungi and animals can be harmful to humans and useful to plants. The widespread use of pesticides in agriculture increased the public concern due to the presence of their residues in the environment and food. Organochlorine pesticides (OCPs) such as DDT and Lindane (γ-HCH) are known as persistent and it is required to control and monitor their residues in the environment (air, water, soil and biota) and food according to the international and national rules.

In 1960-1990, pesticides were used in Uzbekistan in large amounts for increasing cotton yield [1]. This was the cause of environmental contamination by pesticides in the country. Though the application of these pesticides in Uzbekistan was banned (DDT since 1983 and Lindane since 1991), their residues are observed in soil until present time due to their high persistency [2]. Control of OCPs in soil near former agricultural aerodromes, warehouses and burial sites is being carried out by State Committee of Nature Protection. Systematic monitoring of these pesticides in soil of agricultural areas in all provinces of Uzbekistan is carried out by Center of Hydrometeorological Service of Uzbekistan (Uzhydromet). Assessment of soil contamination by persistent pesticides residues is the actual task and in this paper the results of pesticides monitoring in soils in Uzbekistan for 2005-2010 have been analyzed.

Sampling

Monitoring sites of Uzhydromet are located in the 107 districts of all provinces of Uzbekistan representing arable soil (under cotton, wheat, and rice), vineyards, horticulture. Soil samples from these sites are collected every year (in spring and in autumn) to analyze residues of persistent pesticides [3].

Methods

The methodology used for analysis of pesticide residues in soils was in accordance with the standard procedures used by Uzhydromet [4,5]. Organochlorine pesticides were analyzed by gas chromatography with electron capture detector (ECD) [4,5].

The analytical procedure for soil samples is as follows: drying until air-dried condition at 20^{o}C; extraction of pesticides with *n*-hexane + acetone; sample cleanup, using concentrated sulfuric acid for elimination of organic substances; drying of extract with sodium sulphate; reconcentration of the extract; and injection of the extract into the chromatograph.

Maximum admissible concentration (MAC) of pesticides in soil for HCH isomers and for DDT and its metabolites is 0.1 mg/kg [6].

Results and Discussion

The wide use of pesticides results in their distribution as most hazardous contaminants in the environment. Under the influence of various factors pesticides are transformed and migrate from soil to other components of the environment.

In Uzbekistan contamination of the environment (air, soil, surface water) by pesticides was a very actual problem in 1960-1990 because of its large use to increase cotton yield [1]. Although the pesticides use has decreased in Uzbekistan for the last 15-20 years, the problem of the environmental contamination by pesticides continue to be actual because of at present new pesticides are used in agriculture [2,7]. Uzbekistan State Register of Chemical and biological plant protection reagents includes more than 180 substances (i.e. pesticides and others) allowed for using in agriculture [7].

The persistent organochlorine pesticides (POPs) can be accumulated in food chain until hazardous levels even if their amounts in soil are very small.

Pesticides residues have been monitored in soils of all provinces of Uzbekistan. According to soil monitoring data, the detection frequency for DDT and associated metabolites in 2005 and 2010 were 92.54% and 90.80% of samples, respectively (Table 1). Concentrations of sum of DDT in soil were between below of detection limit (BD) to 0.498 mg/kg and to 1.47 mg/kg, mean concentrations were 0.072 mg/kg and 0.054 mg/kg (Table 2), the exceeding of MAC were for 22.39% and 13.79% samples, respectively. The frequency of samples with detected pesticides was 33.21% and 35.63% for α-HCH, and 18.66% and 19.05% for γ-HCH in 2005 and 2010, respectively. Concentrations of α-HCH were between BD-0.0065 and BD-0.0231 mg/kg, γ-HCH BD-0.0082 mg/kg and BD-0.0089 mg/kg, respectively. Observed maximum concentration of HCHs in soil was 10 time lower than their MACs. Mean concentrations were 0.0005 mg/kg and 0.0012 mg/kg for α-HCH and 0.0002 mg/kg and 0.0001 mg/kg for γ-HCH, respectively.

Table 1. Frequency of detection and exceeding of MAC of pesticides residues in soils

Year	Frequency of detection, % of samples			Exceeding of MAC, % of samples		
	α-HCH	γ-HCH	∑DDT	α-HCH	γ-HCH	∑DDT
2005	33.21	18.66	92.54	no	no	22.39
2010	35.63	19.05	90.80	no	no	13.79

Table 2. Pesticides residues in soils of Uzbekistan

Year	Concentration, mg/kg					
	range			mean		
	α-HCH	γ-HCH	∑DDT	α-HCH	γ-HCH	∑DDT
2005	0-0.0065	0-0.0082	0-0.498	0.0005	0.0002	0.072
2010	0-0.0231	0-0.0089	0-1.470	0.0012	0.0001	0.054

Spatial and temporal trends in residues of DDT and HCH isomers in soils of agricultural areas in different provinces of Uzbekistan are shown in Fig.1-4.

Figure 1. OCPs residues in soils of Uzbekistan (2005, 2010)

Figure 2. Sum of DDT and its metabolites in soils of Uzbekistan (2005, 2008, 2010)

Figure 3. α-HCH residues in soils of Uzbekistan (2005, 2008, 2010)

Figure 4. γ-HCH (Lindane) residues in soils of Uzbekistan (2005, 2008, 2010)

The results of monitoring data for 2005-2010 show that the concentration of HCH isomers in soils is much lower than the maximum allowable concentration. Concentration higher than MAC is observed for DDT and associated metabolites. Soil contamination by sum of DDT in local level is observed in Andijan, Fergana and Khorezm provinces of Uzbekistan.

Conclusion

The findings of the monitoring data allow to conclude that the concentration of organochlorine pesticides in soil did not decrease significantly during last years [2,3]. High amounts of pesticides residue are observed in soils near former agricultural aerodromes, warehouses and burial sites, according to State Committee of Nature Protection data [2].

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GENASIS: SYSTEM FOR THE ASSESSMENT OF ENVIRONMENTAL CONTAMINATION BY PERSISTENT ORGANIC POLLUTANTS

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Abstract

The current environmental monitoring and research activities produce large quantities of data on all environmental matrices and a number of chemical and biological endpoints. Production of a considerable amount of data has been currently typical for all fields of human activities and concerns environmental research and monitoring. Thousands of projects have been in progress on the national and international level, which generate data that must be administered, processed, analyzed, and interpreted. However, there is a paradox in this situation that we suffer from the lack of representative data, since their production has not been accordingly supported by development of systems that make them accessible for analysis; we currently face the "Data rich but information poor" problem when based on these quantities of data only small part of information is utilized for interpretation or decision support.

The proposed GENASIS system aims in its current version on the problem of persistent organic pollutants and the analysis, visualization and interpretation of data from their monitoring networks. The project exists within the frame of the Stockholm Convention tools and its objectives are availability of a user-friendly system for the visualization and analysis of contamination of all environmental compartments by persistent organic pollutants and evaluation of actual POPs contamination, its long-term trends and seasonal fluctuations. The GENASIS project utilizes data from national and international monitoring networks to obtain as-complete-as-possible set of information and a representative picture of the environmental contamination by POPs. Project outcomes should be useful as an information source both for lay public and experts, as well as for the process of the Stockholm Convention implementation.

Key words: Persistent organic pollutants; expert systém, evaluation of environmental data

Introduction - Stockholm Convention and goals of GENASIS project

The Stockholm Convention on Persistent Organic Pollutants (POPs) was adopted in May 2001 with the objective of protecting human health and the environment from persistent organic pollutants. Parties to the Stockholm Convention are required to develop National Implementation Plans (NIPs) to demonstrate how the obligations of the Convention will be implemented. Taking into account the circumstances and particular requirements of developing countries, in particular the least developed among them, and countries with economies in transition, especially the need to strengthen their national capabilities for the management of chemicals and wastes, including through the transfer of technology, the provision of financial and technical assistance and the promotion of cooperation among the Parties [2].

Stockholm Convention and its articles represents a legal base for the development of global and national monitoring programmes and tools for effective evaluation of the Convention measures. However, we still face the problem with lack of representative data, accessible for analyses, because their production has not been accordingly supported by the development of systems that make them accessible for analysis [3,4]. Information and expert system GENASIS represents an example of contribution to this topic.

System is targeted for managers and environmental scientists working in the field of POPs investigation at all possible levels of this problem (sources, fate, levels, distribution, human exposure, toxicology and ecotoxicology, human and ecological risk assessment). Primary goal of the project is to develop multilayer information system for management of environmental data with special attention to POPs. As a calibration datasets, the system works with accessible sources from the Czech Republic; potentially later from other countries of the Convention. The project aims to serve as scientific, contract-based repository of data provided by participating partners, based on exhaustive audit of data available from the National POPs Inventories, National Implementation Plans and other national sources of relevant information.

Principal aim of these activities is the development of a sophisticated interactive tool, which will offer a sufficiently effective system allowing to search for connections and causations among problems of the environment, public health status, and other fields of human activities [5].

GENASIS in development: primary data used as calibration and training datasets

The GENASIS system is built as a modular structure providing complex services to a wide range of potential users. The initial version of the database launched in 2010 contains data from the long-term integrated monitoring of persistent organic pollutants at the Košetice observatory which is a part of the European Monitoring and Evaluation Programme (EMEP) [6-8], and long-term data from the ambient air MOnitoring NETworks (MONET) in the Czech Republic, Central and Eastern Europe, Africa, Central Asia and Pacific Islands [9-14].

Furthermore, the data from the large-scale monitoring of soil, sediment, and surface water [7,13] have been recently included in a new version the GENASIS system, which is currently launched (see Table 1). Enhanced analytical tools allowing implementation of algorithms for spatial analyses, and modules enabling comparative analyses of multiple substances or matrices will be also introduced [15,16]. Based on the contract signed between RECETOX and the Czech Ministry of Environment, an import of data from external sources will also be initiated in 2011. Compatibility of the GENASIS system with existing databases is crucial in order to assess the environmental patterns, calibrate the

Table 1. GENASIS input data

ID	Network name	Operator	Matrices
I1	AMAP - Arctic Monitoring and Assessment Programme	AMAP	all matrices
I2	EMEP - European Monitoring and Evaluation Programme	EMEP	air
I3	Global Atmospheric Passive Sampling	Environment Canada	air
I4	MONET CEEC	RECETOX, CEEPOPsCTR	air
I5	MONET Africa, MONET Fiji	RECETOX, CEEPOPsCTR	air
I6	MONET Europe	RECETOX, CEEPOPsCTR	air
I7	MONARPOP	Austrian Ministry for Agriculture, Forestry, Environment and Water Ressources	air, vegetation, soil
I8	OSPAR	OSPAR	air, water, tissues
I9	Water monitoring - WFD	Monitoring based on WFD EU in member countries	water
I10	WHO study – milk	WHO	human tissues

indicator systems, and implement the legislation requirements. A fully developed system will serve as an interactive, on-line working, national POPs inventory of the Czech Republic.

Architecture and functionality of the GENASIS system

The system architecture (Figure 1) encapsulates all steps involved in data validation, processing and analyzing. It is ensured by robust set of software components which are interlinked on the basis of conceptual data model. The most important tools are listed as follows:

1. Primary data repository (archive) – import of data from different sources, safe archiving of primary data of participating partners, export of data to higher layers of the system
2. GENASIS data warehouse – comprehensive assembly of databases, extending primary data in dimensions generated by validation and analyses (transformation functions, aggregation codes, external information, space- and time- related coordinates, etc.)
3. GENASIS GIS module – geographic information system supplying functions directly implemented in the data warehouse toolkit
4. GENASIS on-line data browser - on.-line working interactive software facilitating data accessibility to a wide community of users; both widely open and authorized access to the database content is possible in the system
5. GENASIS on-line reporting – interactive reporting system enabling comprehensive reporting over pre-processed data; reports developed specifically for some databases (on demand) are possible as well
6. GENASIS e-learning tools – set of software tools supporting interactive educational case studies or other outcomes with e-based learning content (tutorials, methodical guides, e-courses, etc.)
7. GENASIS web portal – comprehensive umbrella supporting all software tools and facilitating their accessibility (data browser, reporting system, e-learning functions). Portal serves as a platform for communication of project goals, approaches and outcomes.

Combination of many types of data (emissions and releases inventories, monitoring of abiotic matrices, biomonitoring, total diet studies, human risk assessment, food chain contamination) provides an ideal platform for complex multivariate description of analyzed sites from retrospective viewpoint, supplied with prospective identification of risks. Multivariate nature of GENASIS data structure supports a wide spectrum of descriptive and comparative multivariate analyses, suitable for mutual comparison of sites and/or comparison of examined sites with reference data. Protocol processing of reference data (both from time and space point of view) includes comparative modeling and looking for reference-related analogies. Main added value of GENASIS architecture can be seen in the field of data processing, namely in the following aspects:

- **Hierarchical structure of system components advances the data analysis.** The conceptual model intrinsically distinguishes hierarchy of data descriptors which facilitates implementation of tools focused on data analysis and knowledge mining. Using the hierarchy of descriptors, data and meta data repositories, we can easily decide whether the data are useful for a particular analysis.
- **GENASIS supports robust reference comparison of values.** Regarding data analysis, very important attribute of the proposed system is incorporation of measurement level and its characteristics. Validity criteria reflect some precision measures as well as reference values or protocol standards. A measured value cannot be interpreted and analyzed without reference to a defined measurement standard.
- **Stratified analyses and integration of different data sources.** The multilayer information system supports processing of environmental data from various sources, followed by subsequent validation, advanced analyses and spatial presentation supported by the geographic information

systems (GIS). Hierarchical relationships between primary data repository and data warehouse potentiates automated SW tools and functions.

The functionality of the GENASIS system is optimized for the fields of environmental risk assessment, scientific analyses of environmental data, and as expert information service for managers and institutions on the national, regional and global levels. It provides user friendly analyses for both expert and non-expert users. In addition to it, targeted presentations of data could be produced automatically on request.

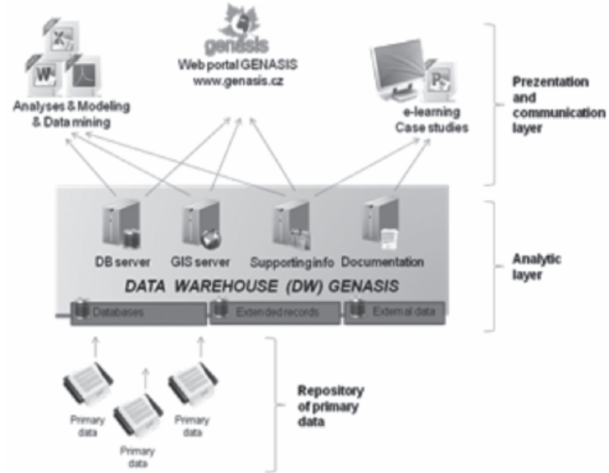

Figure 1. GENASIS system architecture

Users interface

Web interface follows current standards. The example is shown in Figure 2.

Figure 2. Entry page of the GENASIS system

Conclusions

The presented system GENASIS (The **G**lobal **EN**vironmental **AS**sessment and **I**nformation **S**ystem) represents a case of the new generation of software for the visualization and analysis of different data levels. An advantage of the system is a possibility of combination of data from different sources based on a universal data model that may be filled from any database. The system will also be applicable in the risk situations management due to automatic mode of data processing. System expert tools enable use of external information sources and knowledge including panel of experts' entry within the solution of specific problems. Different levels of information service will be ensured by modern web technology. Modern GIS methods will be applied to the project solution using technology of shared map servers. The actual version of the system GENASIS is available on the website [1]. Any comments are welcomed.

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SESSION 6. TOOLS FOR THE ASSESSMENT OF PESTICIDE SITES

POPS SITE ASSESSMENT WITH THE SWIFT SITE ASSESSOR, A NEW COMPUTER AIDED TOOL FOR SITE ASSESSMENT AND MANAGEMENT

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Due to the severe environmental impact of many POPs sites in the EECCA region, there is a need for cost effective, sustainable solutions for POPs site assessment and management. This requires a thorough understanding of the risks and suitable remediation technologies. TAUW proposes use a new computer aided tool to set up a site specific conceptual site model (CSM) to facilitate site assessment and management. A CSM visualizes available information about a site in a schematic structure and makes it easier to assess a site with a very limited amount of site specific information. This new computer aided tool for site assessment, the swift site assessor, SSA, enables the users to actively set up the CSM of a specific POPs site. Cyclic refinement of the CSM can be done very easily after a short training period. Thereby the computer aided tool supports the involvement of local stakeholders. Gaps of information can be identified with a CSM; special elements of the swift site assessor such as automatic signals can support this process. In an iterative process, information gathered in subsequent refinement steps can be integrated easily in the CSM. If used in the framework of an integrated approach for POPs sites as proposed by TAUW, a CSM set up with the swift site assessor can be a valuable tool for better risk assessment, risk mitigation and sustainable management of POPs sites.

Key words: Computer aided assessment tool, Conceptual site model CSM, swift site assessor SSA, POPs site, risk assessment, site management, stakeholder participation, training

Introduction

In many of the EECCA countries POPs sites have severe environmental impact. Therefore there is a need for cost effective, sustainable solutions for POPs site assessment and management. This requires a thorough understanding of the risks and suitable remediation technologies. TAUW proposes the use a new computer aided tool to set up a site -specific conceptual site model (CSM) to facilitate the site assessment and management. A CSM visualizes available information about a site in a schematic structure, it clarifies links between the source and the receptor (e.g. contaminated soil and grazing cattle). This makes it easier to understand what causes unacceptable risks and where actions need to be taken to reduce risks to an acceptable level. An example of a simple conceptual site model is given in Figure 1.

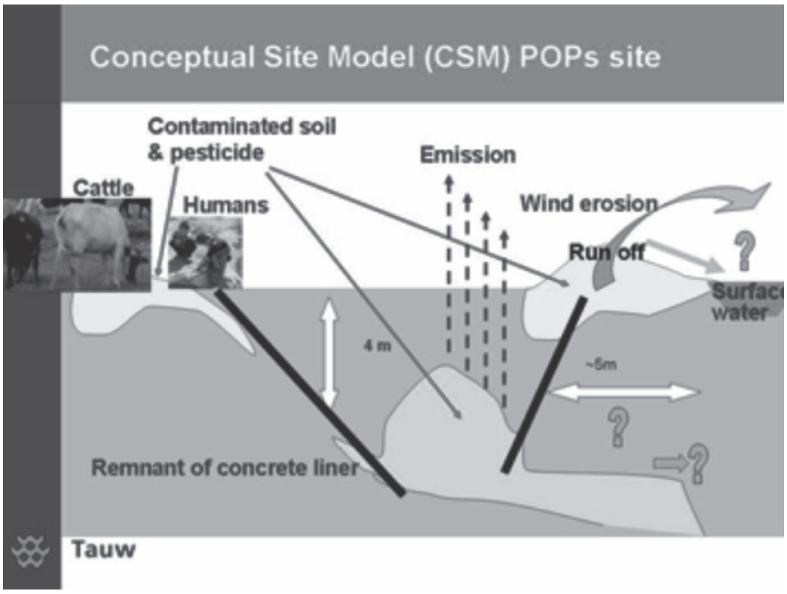

Figure 1. Example of a conceptual site model of a POPs site with source (contaminated soil & pesticide), exposure pathways (e.g. direct contact), transport/contaminant migration (e.g. run off to surface water) and receptors (cattle, humans) and gaps of knowledge depicted with question marks. Graph and photographs: Tauw.

New computer aided tool: Swift site assessor SSA

The new computer aided tool swift site assessor, SSA, can be used to set up a conceptual site model in a simple, standardized way. The SSA is intended to support the assessment of a site even with a very limited amount of site specific information (e.g. if analytical data on soil or groundwater quality are lacking), this is achieved in a stepwise approach, which allows a first risk pre-screening during site walkover. It enables the users to actively set up the conceptual site model of a specific POPs site after a short period of training. As the swift site assessor is a computer aided tool, cyclic refinement of the CSM can be done very easily after a short training period. The pre-screening can be refined in subsequent steps in a stepwise approach, if more site information is gathered. Thereby the computer aided tool stimulates a process of learning and understanding. The swift site assessor has advantages for knowledge transfer and improves current practice of site investigation and site management. It also supports the involvement of local stakeholders. Even though computer based new learning technologies are only technologies and as such do not guarantee better knowledge transfer and stakeholder participation, TAUW feels that using new technologies has an added value for POPs projects. Visualisation can be facilitated by the computer aided tool. The CSM promotes detailed understanding of site characteristics and critical contaminant-receptor linkages, such as contamination of topsoil and agricultural use of topsoil (e.g. cattle grazing on POPs sites with contaminated topsoil). The computer aided tool further promotes the understanding of required measures for risk reduction (e.g. topsoil remediation or change of land-use) and can be combined with other tools for site assessment such as PSMS, the POPs toolkit or the UNIDO contaminated site investigation and management toolkit.

The position of the new SSA tool in the overall process of site investigation, site assessment and site management is given in Figure 2.

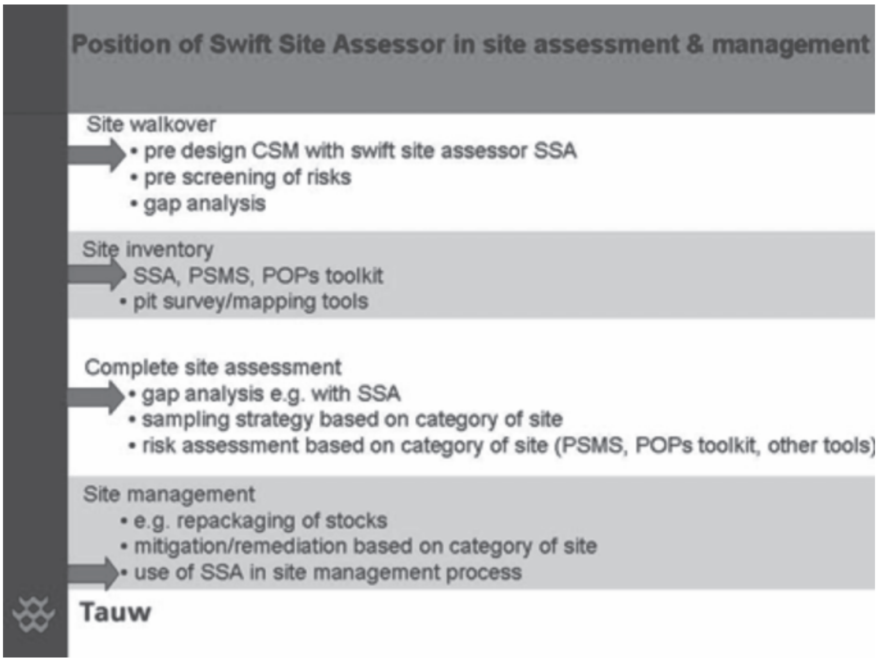

Figure 2. Position of the Swift Site Assessor, SSA, in the process of site assessment and site management

Gaps of information can be identified with a CSM; special elements of the swift site assessor such as automatic signals can support this process. In an iterative process, information gathered in subsequent refinement steps can be integrated easily in the CSM (stepwise refinement from preliminary CSM to final CSM). This feedback loop of CSM set up with the SSA resembles general management cycles, because it comprises elements of conceptional thinking/defining, checking and redefining. Thereby the SSA can support the overall management process of POPs site management.

Conclusion

If used in the framework of an integrated approach for POPs sites as proposed by TAUW, a CSM set up with the swift site assessor can be a valuable tool for better risk assessment, risk mitigation and sustainable management of POPs sites.

The advantages of the computer aided tool are: (1) an easy visualization of the situation at the POPs sites (source, path and receptors) also with a limited amount of site specific information, (2) facilitation of the iterative process of making a conceptual site model, (3) better understanding of potential risks and necessary mitigation measures, during whole process of site assessment and management, (4) simple gathering of specific site information with the computer aided tool for trained field workers, (5) possibility to integrate digital information in other tools (e.g. PSMS), (6) simple information exchange with experts, as information collected can be exchanged among collaborating parties (7) facilitation of mitigation and management measures, guidance of site management process (8) the computer aided tool can also be used for training purposes.

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POPs toolkit. www.popstoolkit.com

UNIDO contaminated site investigation and management toolkit http://www.unido.org/index.php?id=5631

FAO'S PESTICIDE STOCK MANAGEMENT SYSTEM RISK ASSESSMENT OF CONTAMINATED SITES

Richard Thompson and Russell Cobban
UN Food and Agriculture Organisation

FAO has developed the Pesticide Stock Management System as a tool for member countries to assist them in their management of pesticides throughout their life-cycle. The tool is based on a web-based application allied to paper based forms. The application supports two prime functions. The first function supports the management of the **use** of pesticides including: registration, import and quality control, and stock management through the distribution chain to end users. The second function supports the management of **end of life of pesticides** in particular, obsolete pesticides and contaminated materials.

The second function provides tools for the development and implementation of safeguarding and disposal strategies. This includes: the inventory of pesticide materials and the environmental condition of pesticide stores; comparative risk assessment of stores; and their prioritization for remediation. The data gathering forms/questionnaires and comparative risk assessment methodologies are designed to be used by national staff without recourse to external environmental or pesticide expertise and to provide objective results.

The comparative risk assessment methodology is currently based on two risk factors, one for the pesticide materials (Fp) and the other for store conditions and local environment (Fe). The risk factors are calculated automatically using inventory data and the risk questionnaire.

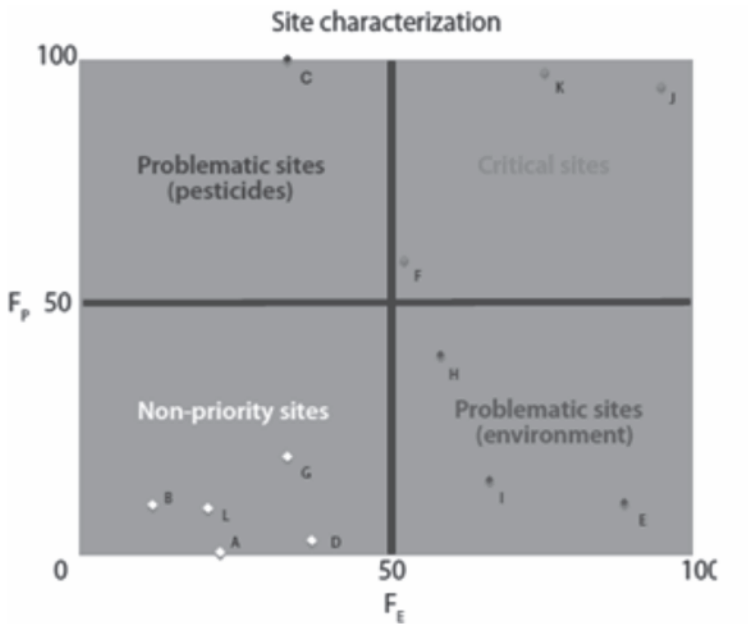
Fp is based on:

- toxicity (WHO classification of the pesticide)
- integrity of the container
- quantity

Fe is based on:

- Condition of the store (integrity of the building)
- Conditions inside the store (storage management etc)
- Environment around the store (settlements, agriculture, water sources etc)

This methodology has proved very effective in allowing national teams to compare the risks between stores and to identify which stores



should be prioritized in any subsequent safeguarding activities. It also assists in the selection of stores suitable for use as collection centres of safeguarded materials prior to transportation to disposal facilities. The detailed methodology can be found in FAO's guidance document "Environmental Management Tool Kit Volume 1 (http://www.fao.org/agriculture/crops/obsolete_pesticides/en/).

This algorithm for calculating risk scores works well for the objective risk assessment and prioritization of above ground pesticide stores by national teams. However the algorithm does not address the risks of contaminated sites or buried pesticides. As the focus of obsolete pesticides initiatives move towards reducing the risks posed by contaminated sites and buried pesticides, FAO is in the process of developing the methodology to better address these situations.

Detailed assessment of a contaminated site is extremely expensive involving the design and implementation of a sampling plan at various depths, chemical analysis, geological survey, mapping, and the development of a conceptual site model to identify the sources, pathways and receptors. Many projects have been completed with only the risk assessments being done and with no interventions to reduce the risks. It is important that projects with limited funds are able to undertake a low cost pre-screening to identify the priority sites, where the funds can be used to carry out the detailed survey and to undertake risk reduction interventions.

The objective of the enhanced risk assessment methodology in PSMS is to allow a national team, with the minimum reliance on expensive external expertise, to undertake this pre-screening. FAO is reviewing existing contaminated site prioritization methodologies to identify the most appropriate or those that can be adapted for this purpose. Amongst those being reviewed are:

- ECOS methodology used in Moldova
- Hatfield/WB
- TAUW
- CCME (as used in UNIDO's methodology)

The methodology will consider 3 factors – sources, pathways and receptors. Each factor will be assessed with a standard questionnaire related to an algorithm that produces an objective risk score. The aim of this enhancement is to allow sites with contaminated soil and buried pesticides to be included in the comparative risk assessment and their prioritization for detailed investigation and subsequent risk reduction strategies. Outputs from the site prioritization tool will be comprised in a graphical and easy to understand format.

A NEW INTEGRAL APPROACH FOR POPS SITES – HOW TO PRIORITIZE POPS SITES

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Abstract

Many POPs sites are sites with severe environmental impact and unacceptable risks to the environment and human health. However, at many sites, investigation, mitigation measures and management of the sites are delayed or stopped due to lack of funding and end up in an infinitive risk assessment cycle.

Based on experience in the EECCA region we propose a new integral approach for investigation, risk assessment, remediation and management of POPs sites. This new integral approach is centred around the conceptual site model (CSM). The CSM is a schematic representation of available information and relevant source-exposure pathway-receptor linkages. Our approach also integrates available tools for site inventory, investigation and risk assessment Costly analyses can be reduced to a minimum. The completed site assessment results in appropriate mitigation and management measures (repackaging, cleaning pits, hot spot removal, remediation).

The new integral approach helps to (further) improve repackaging and site clean-up, supports site management and makes investigation more cost-efficient.

Key words:

Conceptual site model, POPs toolkit, PSMS, risk assessment, site management, swift site assessor, Tegsis soil data management system, UNIDO Contaminated Site Investigation and Management Toolkit

Introduction

For POPs sites in the EECCA region there is usually little site specific information available for a detailed risk assessment of POPs sites, often analytical data on soil and groundwater

quality are lacking. Awareness of the environmental and human health risks of POPs is either lacking and or financial resources for investigation or safeguarding measures are limited. The collapse of national structures has lead to severe deterioration or reuse of many former pesticides storage sites. Currently numerous POPs sites represent unacceptable risks to human health and the environment. For some of the sites in region, acute poisoning of humans and animals has been reported. However, at many sites, investigation, mitigation measures and management of the sites are delayed or stopped due to lack of funding. Delays lead to an infinitive risk assessment cycle (Figure 1), which is difficult to break.

Figure 1. Infinitive assessment cycle (redrawn after Harmsen, 2011)

Based on our experience with investigation and assessment of POPs sites in the EECCA region we propose a new integral approach for investigation, risk assessment, remediation and management of POPs sites.

New integral approach

This new integral approach is based on the conceptual site model (CSM). The CSM is a schematic representation of available site information and is a basic element of the site investigation process; see for example ASTM standard E1689-95 (2008) or Keijzer et al. (2010). The CSM contains information on relevant sources and linkages between sources and receptors (exposure pathway-receptor linkages). The CSM is a tool to clarify which actions need to be taken to reduce risks to an acceptable level and to manage the site.

There are different tools available for the assessment of contaminated sites designed for different purposes. The FAO tool PSMS (pesticide stock management system, see references PSMS) is intended to record and monitor pesticide stocks (inventory) and their usage. PSMS has been developed for stockpiles of pesticides in Africa and has been used in many countries, also in the EECCA region. A more detailed tool, the POPs toolkit (see references POPs toolkit) was designed by Hatfield Consultants and the Worldbank for a thorough assessment of POPs sites in an interactive and iterative process of contaminated site prioritization and site management. The POPs toolkit has been developed for POPs projects in SE Asia, for which detailed site information is needed. Another tool is the UNIDO Contaminated Site Investigation and Management Toolkit. The UNIDO Expert Group on POPs has written this handbook on contaminated site investigation and management as part of a regional project in Nigeria and Ghana. Our proposed integrated approach combines these and other tools into a cyclic process of site investigation, risk assessment, mitigation and site management.

Based on our experience, there are different categories of POPs sites; each category of sites has certain characteristics, which have consequences for the investigation and risk assessment strategy. Some different categories of POPs sites identified in the EECCA region are: storage site with pesticides in store, storage site with buried pesticides, empty stores (contaminated building material mainly), sites with hotspots and topsoil contamination dispersed over large area (e.g. agro-aviation sites).

In our approach we suggest to use the knowledge about the specific characteristics of these categories of sites in order to make the approach more cost efficient. An overview of the new integrated approach for POPs sites is given in Figure 2. During the first site walkover a preliminary version of the CSM is set up. During this step, the site is categorized, e.g. as a store with stocks of pesticide or as a site with pesticides buried in pits. A gap analysis leads to a stepwise refinement of investigation efforts. Depending on the category of sites, further steps (site inventory, complete site assessment and risk management and mitigation measures) are chosen. For a specific site, only those investigation and assessment steps are taken which are necessary for the specific category of sites. For a site with reclaimable pesticides, an inventory of existing stocks can be made using PSMS, for sites with pesticides buried in pits, a pit survey is needed, etc. This means that, by using expert knowledge about the categories of sites, costly analyses and assessment steps can be reduced to a minimum.

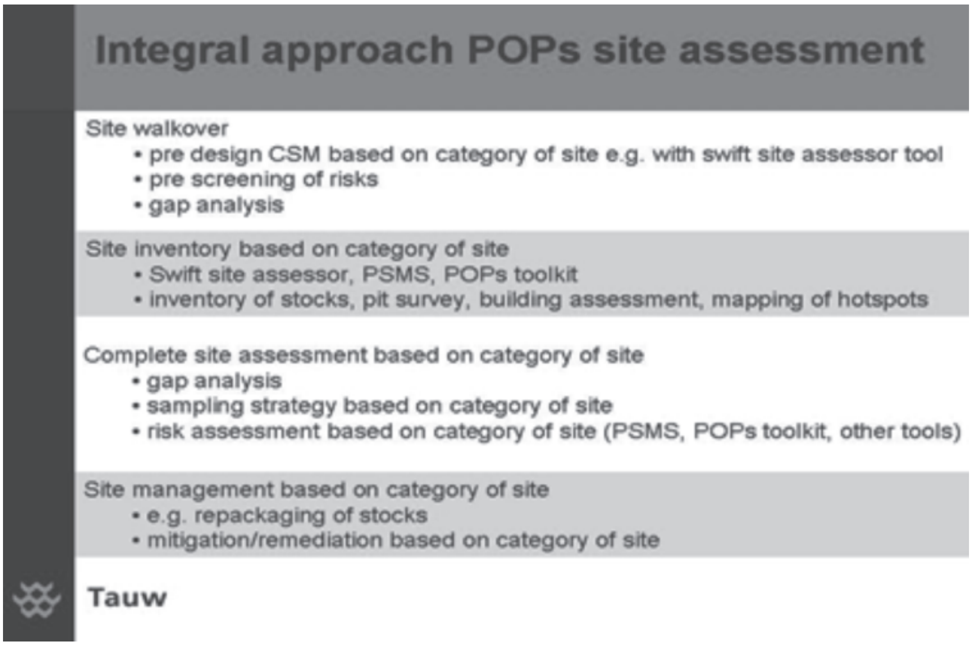

Figure 2. New integral approach for POPs sites based on the stepwise refinement of the conceptual site model integrating different tools for site assessment for different categories of sites

Pre screening of risks at an early stage can help to avoid acute poisonings. The gap analysis can help to avoid, that the site walkover or site inventory is finished too early (prior to gathering the required information). Information of the CSM can then be used for risk analysis with different tools, e.g. the PSMS environmental management toolkit, the POPs toolkit or with other exposure models based on a site specific approach.

The CSM promotes understanding of site specific exposure pathways linking source (e.g. pure pesticide or contaminated soil) and receptor (humans or animals), it visualizes site specific risks and clarifies the need for mitigation measures for the specific site.

The completed site assessment results in appropriate mitigation and management measures depending on the category of site. Existing stocks of POPs pesticides can be repacked for appropriate destruction, pits can be cleaned using suitable techniques, hot spots and contaminated building material can be removed and soil and groundwater contamination can be addressed by suitable measures.

Conclusion

With the new integral approach a preliminary risk assessment is made at an early stage and refined stepwise, integrating several tools. This stepwise integrated approach has several advantages (1) Standardisation of the inventory and investigation process while still allowing a site specific approach. This helps to (further) improve repackaging and site clean-up. (2) Clarification of the (consequences of) specific links between source and receptor and thereby supporting site management. This makes the process more transparent for local stakeholders. (3) Cyclic/stepwise completion of CSM, which allows a site specific refinement of investigation efforts and is more cost-efficient and supports site management.

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PERSISTENT ORGANOCHLORINE PESTICIDES CONTAMINATION OF THE SURROUNDINGS OF RUDNA GORA. RESULTS FROM 2007-2010

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Abstract

The Rudna Gora landfill contains at least 160 POPs. That is the reason why we have systematically monitored the area since 2007. Within the last 4 years we have been taking samples of water and sediments from the bottom of the Wawalnica Stream and Przemsza River, located in the basin of the Vistula River flowing into the Baltic Sea. The results of the analyses indicate presence of large amount of alpha hexachlorocyclohexane (α-HCH), beta hexachlorocyclohexane (β-HCH), lindane (γ-HCH) and isomers of DDT.

GC/ECD (gas chromatography with electron capture detection) was used to determine presence of organochlorine pesticides and for the recent two our years our qualitative results were confirmed by means of GC-MS (qaudrupole mass analyzer). The analytical method was validated.

Key words: Rudna Gora landfill, POPs, pesticide determination, gas chromatography, organochlorine pesticides

Introduction

The „Rudna Gora" landfill contains about 160 thousand tons of waste, including 88 thousand tons of hazardous waste left over after production of plant protection products (including manufacturing of HCH) at "Organika Azot" Chemical Plant in Jaworzno. The landfill is located directly next to the plant, in southern Poland. It was closed just a few years ago. In 2007-2010, Institute of Plant Protection - National Research Institute, Sosnicowice Branch (IPP-NRI) conducted observations of the level of contaminants present in surface watercourses around the area and random testing of wetlands and trenches around the landfill. The testing was performed at the Department of Pesticide Residue Testing, which adjusted its analytical methods to test environmental samples with high concentrations and versatility of contaminants, which differ from the standard tests of pesticide residues routinely conducted by the Department's lab.

This paper is a continuation of the presentation on the Rudna Gora landfill at a previous HCH Forum [1, 2] and shows the results of tracking contaminants present in surface watercourses that carry pollution from the plant and landfill toward the Baltic Sea. It also describes the methods used for preparing the samples for chromatographic analysis and conditions for chromatographic determination.

Site description

The location of the landfill is quite peculiar. It is located on permeable formations, in an area environmentally damaged by mining and a former sandpit quarry. Such conditions make it easy for the contaminants to migrate and pollute adjacent surface waters. Most at risk is the Wawalnica Stream flowing through the plant premises which drains into the Przemsza River valley and joins the river about 1.5 km away from the landfill. Przemsza is a tributary of the Vistula River, which flows into the Baltic Sea.

At the Plant, the Wawolnica stream collects the treated sewage water released from the Plant's water treatment facility. The level of contaminants in the stream is monitored by the Plant at 6 different locations. Additionally, independent monitoring is performed by the Provincial Inspection of Environmental Protection, supported by IPP-NRI at two locations: Wawolnica - bridge in Leg above its estuary into Przemsza and at Przemsza - at the "Jelen" water marker below the Wawolnica estuary (Fig. 1).

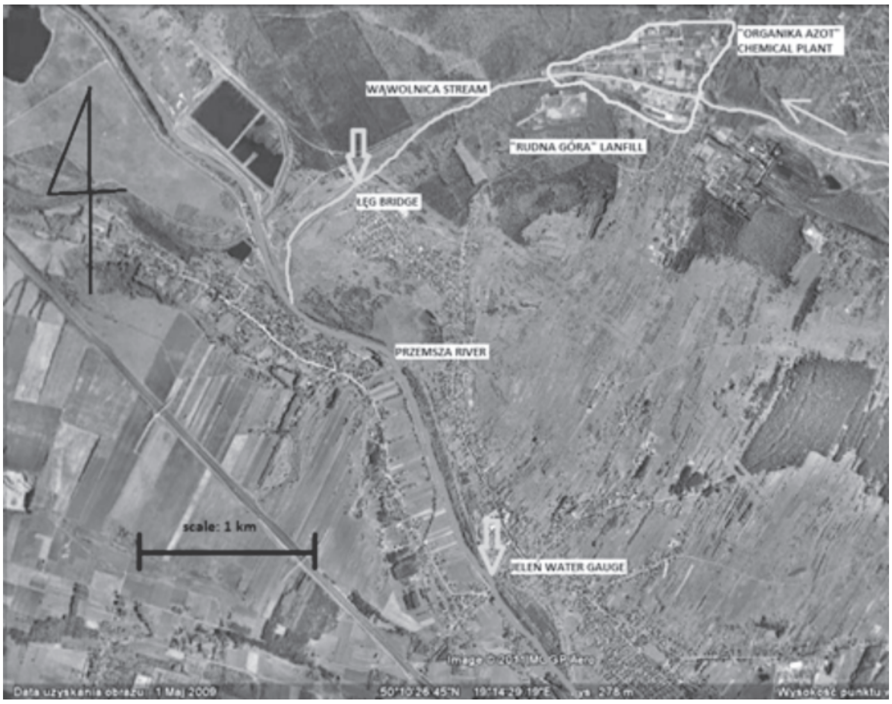

Figure 1. Water sampling locations.

Until 2009, the Wawolnica stream was also collecting water coming from the trenches around the landfill on the south side. In April 2009, the Plant completed a project involving installation of a gate cutting off water flowing from the trenches to the Wawolnica stream and redirecting landfill leachates to a retention pond and then to the Plant's water treatment facility. [3]

Testing methods

Preparation of water samples

A 500 ml analytic sample of water is taken from a larger water sample. After being placed in a separator, 10 ml of saturated sodium chloride solution is added to the sample. The mix undergoes double extraction with dichloromethane in the amount of 100 ml and then 50 ml to isolate the active ingredient present in the mix. About 5 minutes after shaking, the bottom organic layers go through a filter with ahydrous sodium sulfate. The extract is then dried in the presence of sodium sulfate, then placed on a rotary evaporator to dry out completely. The dry residue is dissolved in 5ml of acetone. Acetone extract is tested for the presence of chlororganic insecticides.

Preparation of sediment samples

A 20 g sediment sample is dried for 3 days in room conditions, and then initially shaken for 1 hour in the presence of 100 ml acetone, after adding 1 ml of deionized water. After about 10 minutes the extract was decanted. Then, 100 ml of deionized water and 10 ml saturated sodium chloride solution are added to the filtrate. The mix undergoes double extraction with dichloromethane in the amount of 100 ml and then 50 ml. About 5 minutes after shaking, the bottom organic layers go through a filter with ahydrous sodium sulfate. The extract is then dried in the presence of sodium sulfate and placed on a rotary evaporator to dry out completely. The dry residue is dissolved in 5ml of acetone. Acetone extract is tested for the presence of chlororganic insecticides. [4]

The extracts were analyzed using GC. In order to obtain a satisfactory separation of active ingredients, capillary column and programmed temperature increase were used. The results of GC and column parameters are illustrated below:

Chromatography conditions:

Gas chromatograph: Agilent 6890

Column: HP-5 (30m x 0,32 mm x 0,25 µm)

Detector temperature µECD: 300ºC

Dispenser temperature: 250ºC

Temperature program: Tp-100˚C to 180˚C w/ increase rate of 5˚C/min, retention time 1 min, from 180˚C to 260˚C, increase rate 10˚C/min, retention time 2 min, from 260˚C to 280˚C, increase rate 20˚C/min, retention time 7 min,
Total analysis time: 38 minutes.
Injection type: Splitless
Amount of injected sample: 2µl
GC/MD was used to confirm the qualitative determinations of substances in the extracts of acetone sediments and water. Following are the parameters of GC analysis.

Gas chromatograph Agilent 7890A with MD
Capillary column HP - 5MS UI (30 m × 0,25 mm × 0,25 µm film),
Detector temperature: MS: 230˚C
Oven temperature: 70˚C
Total flow rate 34 ml/min
Dispenser temperature: 250˚C
Total analysis time: 52 minutes.
Injection type: Splitless
Amount of injected sample: 1-5µl

Determined substances - detection limits, average recovery values

The analytic methods used for the testing were verified by conducting a thorough method validation. Limits of determination were set and recovery values were checked. Calibration curves for the test substances ranged from 0.01 to 1 µg/l for water and from 0.001 to 1 mg/kg for sediments. Table 1 presents a list of active substances that were detected, detection limits and average recovery values obtained for the three fortification levels (from 0.01 to 5 µg/l for water and from 0.001 to 5 mg/kg).

Table 1. List of active substances that were determined, limits of determinability, average recovery values obtained for the sediments and water.

Active substance	Detection limit for sediments [mg/kg]	Average recovery values for sediments [%]	Detection limit for water [µg/l]	Average recovery values for water [%]
Aldrin	0.0001	89	0.05	83
pp\`DDE	0.0002	109	0.02	105
pp\`DDD	0.0005	92	0.05	110
op\`DDT	0.0005	97	0.05	90
pp\`DDT	0.001	91	0.10	87
Dieldrin	0.0001	90	0.01	87
α-HCH	0.0005	107	0.01	73
β-HCH	0.0005	97	0.01	86
γ-HCH	0.0005	102	0.01	82
HCB	0.005	98	0.01	85

Results

Tables 2-5 show the results of tests performed on water and sediment samples taken from two locations: the bridge in Leg and Przemsza River by the “Jelen” water marker. Water samples from these locations were collected until 2007. At the same time, water and sediment samples were being collected. Systematic monitoring indicates high levels of POPs. Such a high concentration of active ingredients made it necessary to dissolve the samples multiple times as well as look for organic pollutants (in particular in the sediments).

Table 2. Results of water analyses for samples taken from Wawolnica river by the Leg

Active substance	05.12. 2007	10.06. 2008	05.11. 2008	12.05. 2009	24.11. 2009	09.03. 2010	07.06. 2010	29.06. 2010
	µg/ml							
Aldrin	0.383	bdl	0.121	bdl	bdl	Bdl	bdl	bdl
ΣDDT	23.74	1.03	0.112	0.020	0.770	0.074	9.30	3.33
Dieldrin	bdl	bdl	bdl	bdl	bdl	0.019	bdl	bdl
α-HCH	281	22.63	31	1.74	6.83	7.49	36.3	12.7
β-HCH	113	9.22	10	1.88	2.57	3.65	5.19	5.46
γ-HCH	378	6.66	190	3.38	3.34	4.86	32.6	7.13
HCB	1.98	1.45	bdl	bdl	bdl	0.285	bdl	3.10

bdl – below detection limit

Table 3. Results of analyses of sediment samples taken from the bottom of Wawolnica by the bridge in Leg

Active substance	05.12. 2007	10.06. 2008	05.11. 2008	12.05. 2009	15.12. 2009	29.06. 2010
	mg/kg					
Aldrin	bdl	bdl	0,029	0,039	0,090	bdl
ΣDDT	0.395	0.225	2.46	12.4	7.89	0.373
Dieldrin	bdl	bdl	bdl	bdl	bdl	0.050
α-HCH	1.59	0.830	3.027	0.616	4.23	0.124
β-HCH	0.437	0.184	0.952	5.55	6.25	0.134
γ-HCH	0.380	0.052	0.858	0.495	0.430	1.85
HCB	0.239	0.013	bdl	bdl	1.01	0.050

bdl – below detection limit

Table 4. Results of analyses of water samples collected from Przemsza river at "Jelen" watermarker

Active substance	05.12. 2007	10.06. 2008	05.11. 2008	12.05. 2009	29.06. 2010
	µg/ml				
Aldrin	bdl	bdl	bdl	Bdl	bdl
ΣDDT	0.242	0.244	0.029	0.085	1.02
Dieldrin	bdl	bdl	bdl	Bdl	bdl
α-HCH	1.17	bdl	0.818	Bdl	0.02
β-HCH	0.463	bdl	0.062	Bdl	bdl
γ-HCH	1.61	0.055	0.916	Bdl	0.060
HCB	0.05	0.017	bdl	Bdl	bdl

bdl – below detection limit

Table 5. Results of analyses of bottom sediment samples collected from the Przemsza at "Jelen" water marker

Active substance	05.12. 2007	10.06. 2008	05.11. 2008	12.05. 2009	15.12. 2009	29.06. 2010
	mg/kg					
Aldrin	Bdl	0.012	0.0017	Bdl	bdl	bdl
ΣDDT	0.375	0.041	0.062	0.26	0.035	0.075
Dieldrin	Bdl	bdl	bdl	Bdl	bdl	0.037
α-HCH	0.066	0.026	0.072	Pgo	0.086	0.002
β-HCH	0.116	bdl	0.018	0.017	0.070	0.116
γ-HCH	0.152	0.005	0.037	Bdl	bdl	bdl
HCB	0.022	0.005	bdl	Bdl	bdl	0.035

bdl – below detection limit

SUMMARY

Tests of water and bottom sediment samples collected from the Wawolnica Stream (by the bridge in Leg, above its estuary onto the Przemsza River and from Przemsza by the "Jelen" water marker, over 2 km below the Wawolnica estuary) indicate that contaminants are constantly being transported this way toward the Vistula River. The tested samples were found to contain significant amounts of HCH isomers, in particular α-HCH and γ-HCH isomers. The situation has improved somewhat since April 2009, when contaminants from the trenches around the landfill were cut off with a gate installed to prevent them from flowing into the Wawolnica Stream. It did not resolve the problem entirely, since the Wawolnica stream continues to collect contaminants from the Plant's landfill as well as sewage released from the Plant's water treatment facility.

It is crucial to keep up the research by the same lab and apply consistent testing methods to see how the situation proceeds over a longer period of time.

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CONCEPTUAL SITE MODEL AS A BASIS FOR THE ASSESSMENT AND REMEDIATION OF BURIAL SITES

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Abstract

There have been valuable initiatives to solve problems with POPs pesticides recently. Less attention has been paid to the problems of burial sites containing large quantities of POPs pesticides. Problems with the POPs burial sites, however, are very serious. Burial sites cause a more diffuse and wider spreading of contaminants towards the environment than stocks.

Vakhsh burial site in Tajikistan is a good example from post-Soviet countries of such a burial site. The site contains large volumes of POPs pesticides that were mixed with soil and spread around the site, because of the activities of local people that dug up the pesticides to sell them at the market.

The Volgermeerpolder in the Netherlands is a comparable example from Western Europe. The Volgermeerpolder too contains large volumes of POPs pesticides. Both sites actually contain such large volumes of hazardous material that total destruction of the chemicals has become unaffordable expensive.

Instead of expensive waste destruction Tauw and Witteveen+Bos proposed for both sites to work with a risk based conceptual site model as the basis for the assessment and remediation of the burial sites. The risk based remediation solution is a valuable alternative for rehabilitation of the POPs and other hazardous waste sites. This approach provides chances for cost effective solutions. At both sites no significant pollution was detected in the surrounding environment. Direct contact risks can be taken away by removing hot spots for destruction, or by covering them with a clean top layer. The risk based approach does require ongoing monitoring to detect possible pollution early and act if unexpectedly the levels go up.

Tauw and Witteveen+Bos propose a structured Site Assessment in 4 steps with a risk based conceptual site model approach to prepare for rehabilitation, mitigation, remediation measures.

Both the Volgermeerpolder and Vakhsh have proven that the site assessment using the concept of making a preliminary Conceptual Site Model can provide the basis for:

- A reliable understanding of the site
- A realistic basis for the planning of risk based and cost effective remediation solutions.
- A useful tool for site management

Key words: Assessment of POPs pesticides burial sites

Article

There have been valuable initiatives to solve the urgent threats to public health, nature, and environment of obsolete stocks of POPs pesticides in the last decade. In interesting pilot projects more and more obsolete stocks of POPs pesticides from developing countries have been repackaged and removed for destruction in incineration facilities in Europe. Less attention has been paid to the pressing problems of burial sites that contain large quantities of obsolete stocks of POPs pesticides. Burial sites cause a more diffuse and wider spreading of contaminants towards the environment than stocks.

The Vakhsh burial site in Tajikistan contains around 8,000 tonnes of POPs. The POPs are mixed with soil because local people dug up the pesticides to sell them on local markets. As a consequence the amounts of polluted material seriously increased up to about 40,000 tonnes, making the total disposal of all this material too expensive.

Waste mining

The Vakhsh burial site for instance, situated some 120 kilometre south east from the Tajik capital Dushanbe, contains around 8,000 tonnes of POPs pesticides (see Fig. 1). Originally the site was well designed. Under Soviet rule the site was well managed and strictly guarded. Caused by the collapse of the Soviet Union, civil war and economic crisis, however, no funds remained available to keep the management of Vakhsh in place. Local people dug up the pesticides from the trenches to sell them at the market. As a consequence the pesticides mixed with soil and the Tajik government ended up with such large amounts (about 40,000 tonnes) contaminated material that repackaging and removal of all this material for destruction would be too expensive. Similar events with waste mining and degradation of management and maintenance happened at smaller burial sites in the region like for instance at Suzak in Kyrgyzstan and at Yangiariq in Uzbekistan. Comparable large scale burial sites also exist in Europe. One example is the Volgermeerpolder, were 30.000 barrels of pesticides were dumped.

The common characteristics are that a cocktail of hazardous and non-hazardous waste is dumped, the volumes are large and at the time of dumping nobody realized that this would have enormous environmental consequences. The difference is that the management in the beginning was poor in Europe whereas in the former Soviet Republics the management was well organized. Nowadays it is vice versa. The difference is also that at most sites in Western Europe mitigation measures are implemented whereas in the former Soviet Republics the government has so many other pressing short term problems to solve that remediation of the dump sites is low on the political priority list.

Figure 1. Vaskhsh burial site

To tackle the problems of burial sites containing large quantities of obsolete stocks of POPs pesticides the consortium of Tauw, Witteveen+Bos, IHPA and Mileukontakt developed a step-wise approach for the assessment and management of POPs burial sites. This approach includes the formulation of a Conceptual Site Model. The Conceptual Site Model is a visual or narrative report outlining the hypothesis of a complex pollution situation in a simplified way. The Conceptual Site Model is based on a source path receptor analysis to assess the risks of the sites and prioritize necessary remediation measures. On the basis of field surveys and investigations the contaminated area and its hot spots can be located.

The Volgermeerpolder dump site

The Volgermeerpolder dump site and the Vakhsh burial site will be used to demonstrate the effective approach of drawing up a Conceptual Site Model. The Volgermeerpolder is an area of approximately 105 hectares, which in the twentieth century was used as a dump site for large quantities of chemical waste with a total volume of 6 million cubic meters. For instance 30.000 barrels of pesticide production waste were dumped, resulting in one of the most contaminated areas in Western Europe. The Volgermeerpolder (52°44’ N, 5°15’ E) is located 5 kilometres north of the city of Amsterdam, in a marshy polder with shallow groundwater, open water and a deep peaty soil. After a period of planning and designing the remediation of the Volgermeerpolder took 5 years and was finished in 2011.

In a limited number of piezometers and sediment samples from the landfill body itself a typical set of pollutants was detected (e.g. monochlorbenzene, dioxins, and chlorophenols). The pollutants were mainly related to the dump of the pesticide residues and its degradation products. The concentrations in the sediments and groundwater were in most cases extremely high (up to a total sum of 40,000 µg/l). Given the coherent pollution profile in the piezometers and spot samples, a preliminary decision was reached not to make a detailed inventory and investigation in the landfill body itself. The pollution source (i.c. the landfill body) was to a certain extent approached as a black box, although the results of the sampling campaign and some limited historical information were available about the chemical waste which was dumped.

Peaty soil

Despite the large volumes of chemical waste which were dumped at the landfill and the observed contamination of the landfill body itself, no significant pollution was detected in the surrounding environment (the peaty soil, the ground- and surface water) during monitoring period of more than 30 years. After an in depth analysis of the source, paths and receptors a Conceptual Site Model was drafted. On the basis of this model it was assessed that biodegradation of the pollutants inside the landfill body and natural attenuation processes in the surrounding peaty soil were the key determining processes resulting in the prevention of pollution spreading to the surrounding environment. The final Conceptual Site Model of the Volgermeerpolder is given in table 1.

Table 1. Conceptual Site Model for the Volgermeerpolder (reference 1)

Contaminated source media	Exposure routes	Receptors
Waste material 100 hectares with dumped hazardous waste	Direct contact Wind erosion	Wild life
Soil Contaminated top soil	Direct contact Wind erosion	Trespassers Cattle
		Wild life
Surface water	Direct contact	Cattle
Contaminated surface water in trenches	Surface water streaming	Wild life

On the basis of the Conceptual Site Model it was concluded that the environmental conditions were more or less in a status quo and no major changes would occur in the coming decades. The Conceptual Site Model confirmed the decision not to make a detailed inventory and site investigation of the landfill body itself, but to apply intensive monitoring of the periphery of the landfill body. To save cost on the chemical analyses the sum parameter for extractable halogen compounds (EOX) was used to detect POPs pesticide migration. Extensive environmental monitoring during the construction works confirmed once again that environmental conditions were stable.

Permanent monitoring

On the basis of the Conceptual Site Model it was also concluded that a risk based remediation solution was the best alternative for rehabilitation of the site. This approach provides chances for cost effective solutions. Direct contact risks were taken away through the application of a clean top layer. The groundwater was the only potential path for spreading of the pollution into the surrounding environment. For that reason, the migration of contaminants in the groundwater will be permanently monitored. However, over the past decades there was practically no contaminant migration via groundwater due to the peat layer also underneath the site, which was blocking the migration of contaminants.

The Volgermeerpolder remediation project demonstrates that the Conceptual Site Model approach provides chances for low cost site assessments and cost effective remediation/ rehabilitation solutions. However, it has to be mentioned that for the synthesis of an appropriate Conceptual Site Model the availability of well trained professionals on areas as (hydro) geology, risk assessment, soil sciences and site assessment are a prerequisite.

Vakhsh burial site

The Vakhsh burial provides another example how the Conceptual Site Model approach was used to conduct a low cost site inventory and assessment. After the preliminary assessment conducted by the project Consortium, a group of local professionals was trained in the site assessment approach to draw up a Conceptual Site Model. The local professionals refined the preliminary Conceptual Site Model.

Vakhsh is situated in a dendritic valley system. At the lower valleys of this system small streams are present, which are fed with a system of water pipes. These streams are directed towards an agricultural area approximately 7.5 kilometres from the site. Groundwater is not present in the first 100 meters. It is assumed that at the burial site at least a 60 meter thick layer of loess is present. The infiltration rate is low because of the low annual precipitation.

The burial site is located at the floor of a small valley and does receive external surface runoff. At the bottom of the valley the surface runoff leaves the site uncontrolled. At the floor of the valley 41 sarcophagi were constructed. Starting from the seventies of the last century, obsolete and POPs pesticides were safeguarded in these sarcophagi. The current situation is presented in Fig. 2. In the last decade extensive illegal waste mining has occurred. In some of the trenches, the obsolete and POPs pesticides have been almost completely removed for commercial purposes. In other trenches only part of the obsolete and POPs pesticides have been removed by waste miners, mostly young man lacking any personal protective equipment. In a minority of the trenches the obsolete and POPs pesticides are still present.

Cattle drinking water from open pits

The waste mining activities have resulted in the deterioration of the concrete sarcophagus constructions and the damage of original packaging material and finally the mixing of obsolete and POPs pesticides and soil over an extended area of the valley bottom. This has caused the spread of obsolete and POPs pesticides by wind erosion and surface runoff, accelerated by the absence of vegetation cover at the central part of the burial site.

Within a radius of the first few kilometres around this site there are only a few scattered farms located at the lower parts of the valley floors. The total population of this area is most likely limited to a maximum of a few hundred persons. A small group of farmers and their herds visit the burial site on a regular basis. It is estimated that at least 20,000 thousand heads of cattle are depending on the area directly surrounding the burial site. Apart from the limited local population living at the farms around Vakhsh and the illegal waste miners it is assumed that no significant numbers of trespassers will enter the burial site due to its isolated position. However, given the lack of fences, the absence of vegetation and the presence of open pits, people and cattle can have direct contact with the pesticides. Foot prints of cows and cattle dugs were observed in the open pits and there was evidence that cattle were drinking from the pits. The remains of a dead cow were observed on the perimeter of the burial site.

Given the depth of the groundwater and the presence of water lines in the area it is not likely that contaminated natural groundwater is used as drinking water. Wind erosion, surface erosion and run off as well as windblown pesticides (due to the illegal digging) can cause the penetration of pollutants into the surrounding environment on a regional scale. Pollutant can also enter the food chain by direct contact of the cattle at the burial site and uptake of pollutants in the surrounding environment. Field observations provided only limited evidence for wide spread and/or intense spreading of pollutants into the surrounding environment. An overview of the

Table 2. Conceptual Site Model for the Vakhsh burial site (reference 3)

Contaminated source media	Exposure routes	Receptors
Waste material	Direct contact	Trespassers
Suspected 4,000 ton of pesticides among which DDT	Run off	Waste miners
	Wind erosion	Cattle
	Leaching	Wild life
Soil	Direct contact	Trespassers
Contaminated top soil of valley bottom	Run off	Waste miners
	Wind erosion	Cattle
	Leaching	Wild life
Groundwater	Direct contact	Downstream users
Not very likely	Groundwater flowing	
Standing surface water	Direct contact	Trespassers
Contaminated standing water at valley bottom	Run off	Waste miners
	Surface water streaming	Human using this water
		Cattle
		Wild life

Conceptual Site Model used in the risk assessment is given in table 2.

With the Conceptual Site Model drawn up it was concluded that the current situation at the Vakhsh burial site posed a direct and unacceptable threat to public health and the environment. It was advised to implement measures on the short term to reduce the immediate risk, starting with the removal of hot spots.

The preliminary Conceptual Site Model was verified by laboratory analysis. First, analytical results of EOX confirmed the presence of heavily contaminated soil in and near the 41 trenches. The presence of certain pesticides such as DDT was confirmed with a number of specific analyses. Furthermore, analytical results on EOX confirmed the field observations that no wide and/or intense spreading of pollutants into the surrounding environment exists.

Although the laboratory tests were limited to 20 samples, the results were coherent with the assessment of the Conceptual Site Model.

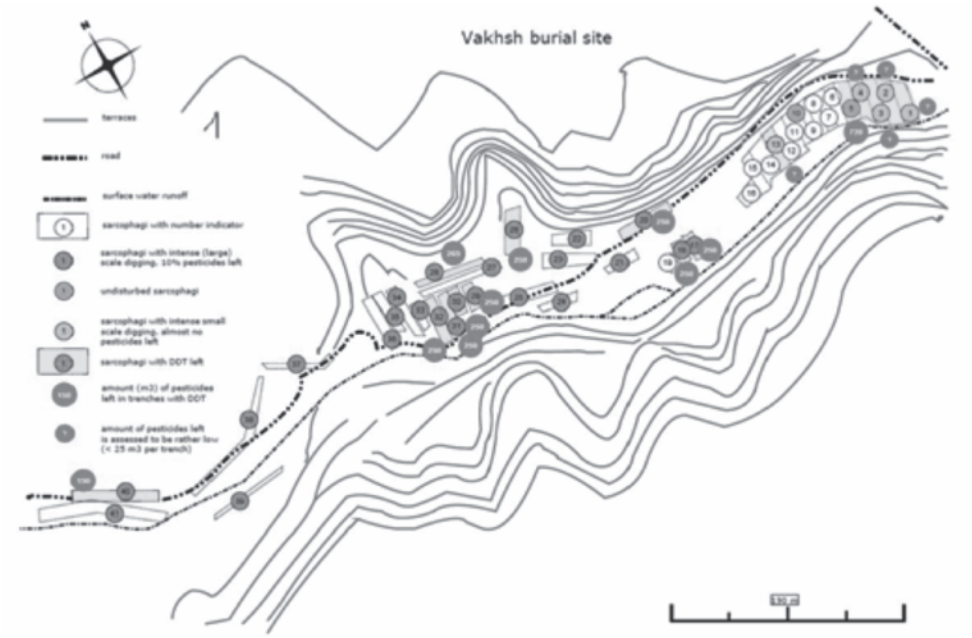

Figure 2. Map of Vakhsh burial site. All trenches have been numbered and colors are assigned reflecting the state; large scale digging (blue), small scale digging (orange), undisturbed (green) (reference 3)

Site Assessment in 4 steps

The Conceptual Site Model assessment approach consist the following steps:

1. Site Walkover
   - Review of historical and background information (e.g. logbooks of burial site and geological maps) and analysis of aerial photographs (e.g. Google Earth);
   - Preliminary Health and Safety assessment for first field visit;
   - Visit to the surrounding environment and walk around at the (safe) perimeters of the site, to observe the general conditions in the field;
   - Determination of preliminary Conceptual Site Model. Perform a gap analysis to assess the focus of the field investigation;
2. Site inventory
   - Based on the gap analyses, plan field visit(s) including limited sampling of the hot spot zones, taking into account all available information, data and observation results;
   - Detailed Health and Safety assessment and planning for visit to the hot spot zones;
   - Field visit to hot spot zones for detailed observations and assessments during initial visit. Take selected samples during the second stage of the visit;
3. Complete site assessment
   - Evaluation and elaboration of a draft final Conceptual Site Model. Perform a preliminary risk assessment to complete the first Conceptual Site Model;
   - Perform a gap analysis with the focus on remediation/ rehabilitation measures of the site;
   - Report the final Conceptual Model including the concepts of the remediation/ rehabilitation options.

Site management

- Selection of rehabilitation, mitigation, remediation measures based on risk reduction, environmental merits and costs
- Implementation of site rehabilitation, mitigation, remediation measures

Steps 1 till 4 can normally be executed within a limited time span. The time needed for the last step depends on the measures to be implemented the time and budget available. Apart form the low costs for the site assessment the Conceptual Site Assessment approach also provides fast results.

Conclusion and recommendations

- The examples of the Volgermeerpolder and the Vakhsh burial site show that the Conceptual Site Model approach provides a basis for low cost and rather fast site assessments.
- Given the extent and nature of both sites a traditional detailed site survey and field investigation can only be organized against enormous costs, in a period of years and only under the umbrella of a full size remediation project.
- At the Volgermeerpolder the Conceptual Site Model assessment results have been confirmed with the results of the successive Environmental Monitoring.
- At both sites the EOX sum parameter has shown to provide reliable results against low costs
- Both the Volgermeerpolder and Vakhsh have proven that the site assessment using the concept of making a preliminary Conceptual Site Model can provide the basis for:
  - A reliable understanding of the site
  - A realistic basis for the planning of risk based and cost effective remediation solutions.
  - A useful tool for site management
- Using the above described method for site assessment of landfill sites, is a valuable addition to the already existing site assessment tools like PSMS, Unido Tool kit, and the Hatfield POPs toolkit.
- Although a Conceptual Site Model can be drafted without any computer model it is recommended to work with some kind of fixed format (e.g. xls evaluation sheet). In this way different sites can be compared in a national assessment and the need for remedial actions prioritized on a national or regional level.
- Furthermore it is recommended to make an inventory of the obsolete and POPs pesticides using PSMS once have been extracted from a burial site during future remediation projects, to facilitate the temporarily safe storage and finally the proper destruction.

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