



GLOBAL EXPERIENCE ON POPS AND OBSOLETE PESTICIDES WASTE MANAGEMENT



SUSTAINABLE MANAGEMENT OF OBSOLETE PESTICIDES IN ETHIOPIA BY THE JOINT VENTURE “POLYECO-TREDI”

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Abstract

In May 2012, the JV Polyeco-Tredi was awarded through international tendering the World Bank funded project for the management of 360 tn of Obsolete Pesticides in Ethiopia. The scope of services included the provision of UN packaging and protective equipment for the safeguarding of a total of 450 tn of OPs identified in the country, and the export and final disposal of 360 tn. During the Project execution, the Project was extended to also include the disposal of the additional quantity of 90 tn safeguarded by the Ministry of Agriculture (MoA). The objective of this article is to share the experience gathered during the execution of the project, the obstacles and contingencies that occurred, and the flexibility that JV showed in order to provide prompt solutions. The disposal of OPs was undertaken in two accredited incineration facilities in Sweden and France, facilitating the potential to provide high quality services to the client at

competitive prices. Moreover, it has to be highlighted, that all types and categories of hazardous pesticides were included in the waste streams and significant problems occurred from the degraded Malathion waste, due to its storage in poor conditions at the Ministry of Health (MoH) storehouses. Malathion waste stream, constituted the main quantity of OPs, exceeding 200 tn, and the JV efficiently tackled the significant problems that occurred during its transportation, in cooperation with competent Port Authorities, Basel Convention focal points and other stakeholders. Lessons learnt from the challenging task, combined with the specific weather conditions and other significant obstacles during the export works in Ethiopia and Djibouti, will be presented for consideration in the implementation of future OPs management projects.

Keywords

Obsolete Pesticides, Ethiopia, POPs, Malathion, Basel Convention, safeguarding.

Introduction

The Ethiopia ASP project was launched in September 2007 following the GEF Funding of 2.62 million, while the Tender for Safeguarding and Disposal Services was issued in February 2012. The goods and services provided within the scope of the JV Project were divided into three parts:

- Supply of goods and materials for the safeguarding by the JV/Project Management Unit of 450 tn of Obsolete Pesticides at different storehouses and locations within the country
- Safeguarding of 186 tonnes of obsolete pesticides at the Ministry of Health Store (Mekenisa main garage) in Addis Ababa and Tigray Regional Health Bureau Stores (TRBH Garage A and B) in Mekele.

- Transport and disposal of 450 tonnes of OPs by high temperature incineration, at licensed facilities in France and Sweden.

Mobilisation

Following finalisation of administrative and contractual procedures, the project equipment and consumables were manufactured in Europe and shipped to Ethiopia in twelve 40' Containers in mid July 2012. POLYECO field experienced personnel comprising two chemical engineers and one foreman arrived in Addis Ababa at the end of July 2012 to start site preparation works. Although equipment arrived at the end of August at Djibouti and despite the fact that the JV and MoA, promptly prepared and submitted relevant customs documentation, the delivery of containers in Gotera Main Garage started at the beginning of September and was finalised at the end of the same month. Containers remained at customs authorities for several days due to customs clearance bureaucratic procedures. Before commencement of safeguarding works, the following procedures were implemented:

- All equipment was set up at suitable places at the site.
- Signs and traffic management were erected as necessary.

- Security requirements were set up, as required for the safe performance of the works.

- Temporary power, wiring and lighting requirements were set up.

- On-site sanitary facilities and water supply was ensured for the contractor.

Work areas were marked and zoned as clean zone, buffer zone or dirty zone, according to EMP.

Specific rules were set up for the different areas and measures applied to avoid cross-contamination between the two areas.

Licensing

Notification Application was prepared and submitted to the Competent Authorities at the beginning of July 2012. Eleven transit and disposal countries were included in the predefined routes specified in the Licensing application for Sweden and seven countries for France. Following notification from the shipping line, that due to huge congestion in the Jeddah terminal, the port of Salalah was lately used as an alternative route, two more licensing applications for Sweden and France were prepared and submitted to Ethiopian EPA

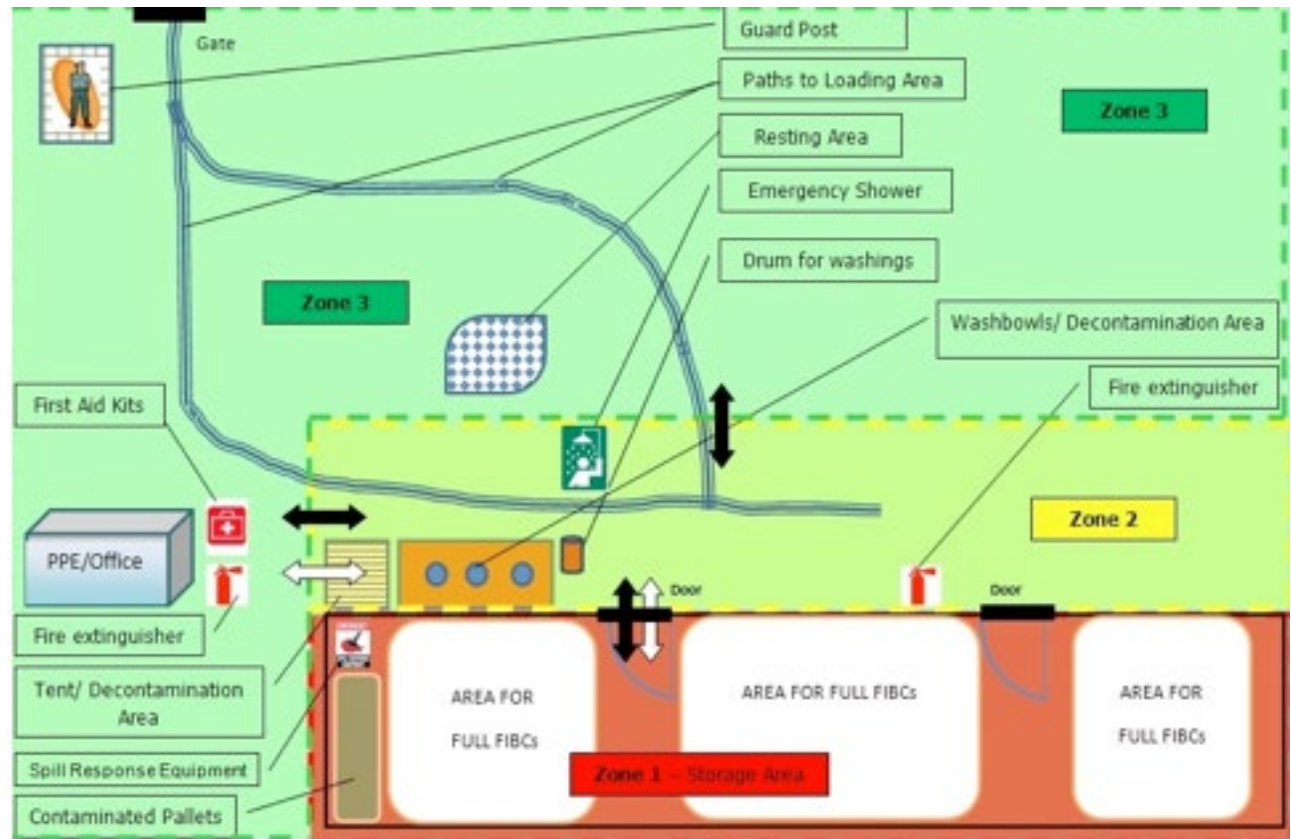
including Oman as transit country, in order to cover all potential changing routes. The Swedish Authorities promptly issued export licenses in early September, and JV actions focused on the issuing of remaining transit countries consent, such as Djibouti and Saudi Arabia. In November, the shipping line suddenly added port of Aden (Yemen) in its scheduled route to Europe, and the JV informed the client that in accordance to the Environment Protection Law No. (26) of 1995, the Republic of Yemen, Article (54), it was prohibited for vessels or aircraft or any other means to enter the territorial waters as a transit passage if they carry radioactive, toxic or hazardous waste, except if prior permission from the cabinet and approval from the parliament was granted. Unfortunately, it was identified that this procedure would last from three to six months and JV, following communication with Basel Convention Secretariat, evaluated all alternative solutions, such as potential utilisation of other shipping lines with already licensed routes and also proceeded to negotiations with the shipping line in order to grant an exception from Yemen port, particularly for the vessels carrying malathion waste. Through numerous meetings with the shipping line, The JV arranged to achieve an exception from Yemen port

for the 1st cargo of OPs from Ethiopia destined to Sweden. Furthermore, it has to be stated that although Swedish Permit was promptly issued, significant delay occurred in the issue of the licensing permit from France. The Notification application was by mistake of the Ethiopian EPA delivered to the French authority responsible for the transit of waste and not for disposal. The JV took immediate action to remedy the situation, prepared and submitted the notification application to the correct authority and only 2 days after a meeting with French competent Authority, the export license to France was also issued, by the end of December. At this point, it has to be emphasised, that the issue of modification of the shipping route was an obstacle that also previous OPs contractor in Ethiopia had faced and did not manage to convince the shipping line to change the route. As a result, in that past case the contractor prepared new TFS, while the JV successfully managed to agree with the shipping line on a route that would not include Aden Port also for the forthcoming vessels, carrying the remaining 150 tn of Ethiopian OPs to France and to Sweden. The final export licenses for the 1st and the 2nd shipment were issued by the Ethiopian EPA in December 2012 and early April 2013, respectively.

Safeguarding

Safeguarding works commenced in mid-August 2012 following facilitation of road clearance to the Site and kind provision of UN approved packaging equipment by MoA. Heavy rain restricted the works at the end of August, since water was entering the storehouse through the roof. Supporting plywood was positioned

on the ground to facilitate the forklift's movement and at a second stage, an auxiliary path was constructed. Due to the difficult working conditions and the necessity to work with high level protective equipment (type 3 Overalls, full face masks), the JV took decision to double manpower in order to accelerate safeguarding works. Repackaging works in Makenisa





Pictures 1-2: Zoning of the Site area and repackaging works commencement

were finalised within 30 days following the commencement of works, and 400 FIBCs and 13 Drums in total were fully packed. Due to space restrictions and poor storage conditions, 271 repacked FIBCs were transported to Gotera Main site for temporary storage. At Mekele store, safeguarding works for 30 tn were completed within three days, and within four days all OPs were transported to Gotera Main Site. POLYECO personnel remained in Addis Ababa, in order to evaluate the safeguarding works conducted by MoA and to provide any additional support requested. Safeguarding works were finalised by MoA by the end of December 2012.

Export of OPs

Following communication with Ethiopian stakeholders, it was decided that the export of OPs would take place in two steps, and corresponding cargo separation will be facilitated. The containers stuffed with repacked pesticides should be escorted by a pick up truck of the Ministry of Agriculture carrying PPE and spill response equipment from Addis Ababa up to the border of Djibouti, and from the border of Djibouti up to the Djibouti harbour the containers should be escorted by national police of Djibouti. The JV promptly proceed with early container booking; however, due to bureaucracy procedures imposed by stakeholders from Djibouti (Chamber of commerce, Custom Authorities etc) the first empty containers arrived in Addis Ababa early in December. Stowage/loading works were initiated, and fourteen containers were loaded with 300 tn of OPs and transported to Djibouti, having Norrköping Port in Sweden as a final destination. The containers were loaded on MSC vessel and departed Djibouti on the 29th of December 2012. Following the issuance of export licence by Ethiopian EPA, the JV booked the first available shipping containers to export the remaining 150 tn of OPs and the cargo was loaded on MSC Vessel on the 2nd of May 2013.

Temporary Storage at Antwerp Port

The 300 tn of OPs arrived in Antwerp Port in February 2013, and odour issues that were identified alarmed the hazmat authorities. It has to be stated that within the 300 tn of OPs, 220 of Malathion waste, produced in 1998 was included. This malathion waste had undergone poor storage condition during all these years and had provoked significant odor issues to the neighborhood of Mekenisa and especially to the students from the nearby school. Malathion has probably undergone chemical degradation due to the long term storage, and although it was packed in accordance with IMDG requirements in UN approved packagings, it was still emitting significant odour. The JV took immediate action by conducting chemical analysis, air sampling, air measurements inspections and negotiations with Belgian Hazmat and Environmental Authorities. Even though numerous meetings were conducted, and Belgian Stakeholders confirmed that the cargo is not posing a threat and granted approval for its loading on board, the shipping company still declined to accept the cargo. Alternative options such as disposal within Belgium at high temperature incinerator were evaluated in cooperation with stakeholders. Following continuous and substantial efforts by the

JV, the shipping line altered its initial decision and, at the end of March 2013, granted its approval for the continuation of the trip to the final destination of Sweden.

Disposal of Waste

Following the approval by the shipping line, all blocked containers in Antwerp Port were delivered to SAKAB at the beginning of April 2013, and the destruction process was initiated. Furthermore, the remaining 150 tn of OPs arrived in France and Sweden at the beginning and in the middle of June, respectively. The destruction process of the 450 tn was finalised successfully by the end of June 2013, before the official project closure, contrary to the obstacles, occurred in such a challenging project.

Conclusions

Based on the obstacles that occurred during the project implementation, the following conclusions derived. These shall be taken into account in future OPs management projects:

- With reference to the licensing issue, it is important that through communication with Shipping Lines, contractor identifies all potential transit countries that might be added in the itinerary of the route in the future. There is a high possibility that predefined route is altered and, in that case,

contractor shall respond immediately in order to achieve potential exclusion as the JV successfully managed.

- Even experienced Competent Authorities may fall into mistakes during the licensing procedure. Therefore, it is essential that the contractor follows the progress of the notification application closely in order to take remedial actions.

- It is preferable that packaging equipment is defined and supplied by the experienced contractor in accordance with project needs. In Ethiopian case study, the type of the packaging equipment for the 450 tn of OPs was predefined by the competent authority as a supply component during tendering procedure.

- Project preparation consultants and stakeholders should take into account the fact that the safeguarding and disposal component in hazardous waste management projects is crucial, and adequate time shall be allocated, especially taking into account various unforeseen parameters may arise during project execution. The Ethiopian ASP project was launched in 2007, and the safeguarding and disposal component was procured after 5 years with a total assigned duration of only 7 months.

- Even unfavourable and unpredicted situations such as the raised odour issue in Antwerp Port can be managed efficiently following consultation and coordination with all relevant competent authorities.

- Development and application of sophisticated logistic plans in developing countries will not ensure the minimisation of delays and demurrage costs, due to the bureaucratic conditions that prevail.

- There are always significant differentiations among the registered OPs inventories and the actual pesticides that the contractor will encounter on site. The worst case scenario in terms of potential hazards shall always be taken into account.

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REGIONAL WORKSHOP ON CONTAMINATED SITES

IN MOZAMBIQUE 2011-2012: EXPERIENCES OF THE DEUTSCHE GESELLSCHAFT FÜR INTERNATIONALE ZUSAMMENARBEIT (GIZ)

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Abstract

To address the consequences of stockpiles and contaminated sites in Southern Africa as an extension of the African Legacy Project under the Global Environment Facility (GEF), GIZ, in co-operation with United Nations Industrial Development Organization (UNIDO) and the International Council of Chemical Associations (ICCA), organized two consecutive workshops in Mozambique in 2012 to build local capacity in the identification, risk assessment, and remediation of contaminated sites in the region. Lessons learnt and a practical guide for authorities to deal with the challenges have been compiled in a short YouTube film, while further projects in co-operation with the private sector are being planned. The article gives an overview and draws conclusion from the experiences in Southern Africa while making a case for future involvement in land recycling.

“There has been hardly any progress over the past decade in Africa, where 50,000

tonnes of stockpiles has an estimated management cost of US\$250 million” (Weber, Vijgen, Aliyeva 2012: The need for an integrated approach to the global challenge of POPs management). The effects of such stockpiles, as well as former industrial sites, for which the same statement holds true, will be felt in the future, with marked impacts on arable land in Africa due to simultaneously growing populations as a challenge to food security and industrialization causing future competition for land use.

As a contribution to the issue described above, and in the context of its mission for the German government and a member of the Global Alliance on Health and Pollution (GAHP) to rid the world of the negative health impacts of hazardous chemicals, specifically affecting the vulnerable population in Least Developed Countries (LDCs), the Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) with the Sector Project on Chemical Safety

(ChS) initiated a series of workshops to date in Southern Africa, based in Mozambique with 17 participants, mainly from Mozambique, but with several from South Africa, Lesotho, Swaziland, and Uganda, between March and December 2012.

The Workshops

GIZ, UNIDO and ICCA decided to stage a training workshop, UNIDO covering travel expenses and ICCA and GIZ covering expenses related to the workshop itself, as an extension of the GEF-sponsored capacity strengthening and technical assistance endeavours for the implementation of Stockholm Convention's National Implementation Plans in African LDCs¹, pro-

¹ Section 1(e) of Article 6 of the Stockholm Convention states that Parties would “endeavour to develop appropriate strategies for identifying sites contaminated by chemicals listed in Annex A, B and C; if remediation of those sites is required it should be performed in an environmentally sound

viding technical assistance and expertise in the management of contaminated sites in the form of a pilot demonstration for the local experts in the region on dealing with (potentially orphaned / legacy) contaminated industrial sites.

In the first workshop, the basics were laid by introducing the theoretical principles of assessment and management of contaminated sites, having already compiled a cadaster (land registry) of legacy sites in a country. The second workshop on the topic “Identification, preliminary evaluation and inventory of contaminated sites” (10-12 December, 2012) took the theoretical considerations to the field with a practical, hands-on experience session at Dondo Im-

manner”. This implies that countries which ratified the Convention will need to rehabilitate sites contaminated with POPs chemicals. The LDCs in Eastern and Southern Africa which are parties to this Convention are therefore required to develop appropriate legislative framework and then importantly a strategy to identify sites contaminated by POPs chemicals. Many countries in the region have recognized the problem of sustainability that POPs projects would face when they deal only with the disposal of stockpiles ignoring the related problem of subsequent clean-up and remediation of contaminated sites. Thus, Component 3 of the project aims at introducing appropriate strategies for identifying sites contaminated with POPs and ensuring effective planning for the implementation of remediation measures to clean up contaminated sites.

pregnation Plant in Beira, Northern Mozambique on the 14th of December. The overall intention was to clearly prioritize activities nationally and break the infinite assessment cycle, based on environmental and economic grounds and in accordance with the national situation and legal framework.

In the earlier workshop, there had been site visits to three potential legacy contaminated sites in Matola, 20km outside Maputo, including a leather factory near a river, relevant for the health impact, and a dumping area from a fertilizer factory then used to recycle scrap metal. Day two consisted of various presentations, including local examples of dumpsites and one by German expert Dr. Frieberthäuser on the principles of investigation, risk assessment, remediation and monitoring of contaminated sites in Germany, serving as the basis for discussing the principles of contaminated sites management, specifically the identification process, also featuring prominently in the film².

On day three, discussions of the case studies presented continued. ICCA experts then used the leather factory that the participants had visited on the first day as a model site to simulate the application of

² The film can be found under <http://www.youtube.com/watch?v=XPGi-IOlwA8>

the principles of contaminated sites management. The afternoon programme was reserved for a case study designed ad-hoc by the experts in order to create a case from scratch and walk the participants through every phase of remediation. With the site still fresh in memory, the exercise helped the experts to better understand comprehension gaps of the participants. The selected site was a tannery visited by the group on day one.

It is essential to start off by analyzing a legacy contamination³ by carrying out a socio-economic impact⁴ and risk assessment of contaminated sites, assessing the capacities of the existing laboratories, pos-

³ A “legacy contaminated site” is a historical legacy from former industrial activity conducted when there were few, if any, environmental regulations in force. The nature of the contamination varies greatly, from heavy metals to hydrocarbons and organic chemicals. Water contamination occurs largely as a result of rainfall flushing chemicals, contaminated sediment, and dissolved compounds into nearby streams or the groundwater beneath a site, e.g. where there is poor storage and spillage due to poor handling of chemicals such as solvents or oils. Contaminants upon entering the water environment can affect even distant receptors.

⁴ Former polluters, often small- and medium-sized enterprises where the original polluter can no longer be identified to pay for the remediation, negating the effectiveness of the “polluter pays” principle.

sibly organizing training and awareness building workshops for national experts, decision makers and other stakeholders.

After that initial phase, a site-identification has to take place. The aim of this phase is to identify and assess the potential level of contamination potentially presenting a risk at the site. The Environmental Site Assessment encompasses preliminary investigations including review of historical sources (like photographs, maps, etc.), review of regulatory records and physical setting information (topography, geology, etc.), interviews with (former) owners, occupants, neighbours etc., a visual survey of the site, conclusions, and recommendations with associated cost estimates.

During the Site Assessment phase, questions about the (potential) defined source of contamination (e.g. size, location), pathways (including the reach of the contaminant) and the receptor (human, environmental, special cases like nature reserves) of concern have to be addressed. A Qualitative Risk Assessment, i.e. developing a conceptual model identifying potential pollutant linkages, consists of a desktop study to assess the level of contamination that could present a risk at the site⁵. Conceptual site models are an essen-

⁵ Understanding the history of a site is crucial to understanding the potential for source contaminants to be present. A site containing contaminants

tial element of the assessment and present possible connections between identified potential contaminant sources, pathways and receptors. A risk assessment includes (risk-based) decision-making and its consequent actions, e.g. which problems need to be dealt with most urgently or the decision for a certain remediation measure over another.

These theoretical and more superficial first steps are followed by a deeper Soil and Groundwater Investigation based on soil borings and sampling (chemical / physico-chemical analysis), groundwater sampling, followed by another, now more detailed risk assessment⁶ or a Site-Specific Risk Assessment with the linkage of pathways, receptors and (planned) use⁷ of the

may not cause significant harm to a receptor in its existing use, but where a development (a new use of the site) is proposed there is the possibility that significant pollutant linkages will be created. Therefore, it is important that low risks identified in this phase are not discarded entirely from the assessment process. The usual approach to risk assessment examines the source of contamination in relation to the receptor.

⁶ By carrying out a detailed risk assessment, it may be possible to reduce the scope of site remediation works required. Quantitative Risk Assessment is a stepwise approach, sequencing ever increasing data quality with site investigation, samples, laboratory results, comparison of results with science-based guideline values etc.

⁷ For example, a human health risk assessment for

(potentially) contaminated land, still using the generic quantitative models.

Following this, countermeasures have to be evaluated, including source reduction (e.g. excavation of hotspots and removal of a leaking tank and the surrounding contaminated soil), pathway management (e.g. using a barrier to restrict the flow of contaminated water), and modifying exposure of the receptor (e.g. by choosing a future land use where opportunities for exposure are reduced). Often the easier and cheaper solution may be preferable to a technologically complex, though more thorough solution, depending on the risk involved and the (prospective) land use.

Remediation based on a feasibility study and a cost-benefit-analysis⁸ must be carried out where there are unacceptable risks

a residential development requires near-surface soil sampling. Where contamination of groundwater is suspected – thus again affecting humans and the ecosystem – the risk assessment is likely to require an assessment of contaminant mobility in the soil.

⁸ While investigating a potential contaminated site, special attention must be paid to the overall cost which includes: site assessment costs (initial investigation) to risk assessment costs to clean-up costs. The conventional approach is that lower investigation costs give rise to higher clean-up costs, while spending more time and money during the investigation stage and hence more precision leads to lower clean-up costs.

to health or the environment in relation to the current or intended use of the land and its wider environmental setting, e.g. in order to protect human health and the environment or enable redevelopment. Generally, remediation activities are measures taken to eliminate or reduce pollutants/contamination (decontamination measures) or to inhibit or reduce the expansion of contamination without removing it (containment measures).⁹ The preferable method depends on the substances present¹⁰ and their concentration, as well as external factors. In all remediation measures, appropriate personal protection equipment and other safety measures must be applied as per usual.

9 They include excavation, secured relocation of material, containment (lining, in-situ sealing systems, cover systems, Permeable Reactive Barriers (PRB), or solidification with reagents to immobilize the substance, e.g. hexavalent chromium transformed to trivalent chromium), treatment-based remediation including pump-and-treat and / or long-term groundwater monitoring

10 E.g. carbon adsorption for pesticides, air stripping for CHC incl. vinyl chloride, BTEX etc., biological purification processes (aerobic, anaerobic, co-metabolism by addition of methane) mainly for CHC, chemical oxidation (by hydrogen peroxide or ozone) for CHC, phenols, pesticides, cyanide, or ion exchange for heavy metals or cyanide. Water filter units with activated carbon can also be applied.

The practical part of the second workshop with site walk-through and interviews of persons familiar with the site, a historical search on the site's use, including historical and current aerial photographs and archives of relevant authorities, and gathering of soil, hydrologic and geologic data on-site gave valuable practical experience to the local experts in combination with experiences from the international experts.

Another relevant point is the continued enforcement of adherence to threshold values (sustainability element) on sites currently being used to prevent the creation of further contaminations.

Concerning the actual health and environmental risks encountered on-site, it was established that the impact risk for groundwater was particularly high, as the depth of the groundwater was only 2m below the ground level according to site personnel, resulting in the infiltration of impregnating oil through unsealed soil into the groundwater, with a drinking water well only 100 m away. Additionally, gaseous emissions into the atmospheric air occurred due to all process steps taking place outdoors, resulting in the percutaneous and inhalative exposure of workers.

Lessons to be learnt

Even simple steps like interviews with neighbours or employees can lead to useful results without any chemical analysis. By performing a thorough preliminary investigation, laboratory analyses – which are very costly contexts like Mozambique's – can be partially avoided. Several on-site test procedures are available for an initial evaluation of an area of potential concern or contaminated site, some of which are low-cost and straightforward. Numerous contaminations are for instance immediately recognizable by their colour, oily luster, or by a characteristic odour of the soil / water. E.g. originally colorless oil generates a green respectively black coloration of the soil as a result of the partial microbial degradation.

The workshops showed that even larger enterprises sometimes fail to apply sound chemicals management, even where population's drinking water supply is affected.

Even well-trained and competent representatives of the governmental environmental authorities, who are also sensitized to the dangers of hazardous chemicals, do not always have the analytical methods needed to analyze unknown chemicals. Even with minor investments in equipment and pertinent instructions, improvements in the

management of hazardous chemicals can be achieved.

Conclusions

According to World Bank data¹¹, it would take 100 years at the current rate to complete the necessary clean-up activities in Africa regarding stockpiles, which means that plainly more has to be done. More urgently, contaminations from these and orphaned industrial sites must be stopped in order to negate increasing negative health and environmental impact. In order to achieve this, several elements must be taken into account:

Firstly, a comprehensive legislation (nota bene: incl. at precautionary level) must be the aim, as positive European experiences show. Moreover, high-end measures and simple solutions can equally contribute to the process. Regional co-operation and co-ordination to that effect is invaluable specifically for countries catching up on the necessary steps.¹² To this end, capacity

11 Following Weber, Vijgen, Aliyeva 2012, using data from: World Bank (2002) Africa: Africa Stockpiles Program (ASP): funding the prevention and disposal of obsolete pesticides from African countries. Work Program Inclusion-Resubmission (FAO-World Bank Co-Submission), New York.

12 The same goes for the connection with sound general chemicals management, improving knowledge and expertise on preventive and remediating

building programmes tailored to the specific needs of the target groups (e.g. SMEs and governmental authorities) have to be developed and implemented in the selected countries. By doing so, the main targets are to help develop technical capacities of local actors for future clean-ups, but include training materials on sustainable chemicals management, as opposed to one-off measures, and identification of viable financing possibilities for the partner countries to clean up contaminated sites.

With financing generally constituting the bottleneck, hinging itself on (political) will of stakeholders and governments, the central question is about the possible entry point for the intended projects. Also, competition for the resources and duplication of the efforts where money is actually available has to be avoided through constant open communication.¹³

actions in equal measure. The result is a holistic approach to chemicals management in all its aspects.

13 This kind of spirit of co-operation, as envisaged in South Africa, can even lead to shared use of practical yet costly equipment which any one stakeholder alone could not afford. It is important to consciously take note of these possibilities in the analysis from the very beginning.

Reflection on the correct entry point
Individual trainings for authorities or companies may have some immediate impact, but unless there are regulations in a legal framework as well as enforcement or incentives, it will not be sustained. Backing from policy makers and the society at large is thus paramount to create sustainability, for which good public relations work is relevant. Hence, a concerted effort on all of these levels between all relevant stakeholders is needed. What needs to follow projects like the one in Mozambique is a continued process of coordination based on communication and shared or complementary activities. A concerted effort thus consists of communication and co-ordination of efforts of stakeholders (as opposed to a competition scenario), as well as prioritized, meaningful (i.e. sustainable) and impact-oriented actions.

On the financial side, it should be noted that clean-ups / site-remediations are not an attractive topic for investors. However, especially in growing and industrialising Developing Countries, land recycling for various types of land-use and to relieve pressure from (future) competition for land, constitutes an increasingly appealing topic due to its economic benefits for companies and city planners, especially due to the frequently convenient location

of legacy sites on the outskirts of growing cities and on the margins of the potentially arable land of the dwindling rural areas. All of these elements make land recycling a useful starting point for future activities in the sector.

OBSOLETE PESTICIDE MANAGEMENT IN AFRICA; THE AFRICAN STOCKPILE PROGRAMME (ASP)

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The legacy of Obsolete Pesticides is not only related to near Eastern and Central Asia countries. In Africa the widespread presence of Obsolete Pesticides has created problems for more than 20 years. According to information from FAO the quantities in Africa amount to 27,395 tons compared to the EU recorded quantity of 241,000 tons for Eastern Europe (2006).

The environmental and health risks posed by the existence of Obsolete Pesticides in Africa are serious. In response to concern over these risks the ASP was established. The ASP is a Partnership initiative with the overall objective of mobilising international funding and technical support to eliminate the existing stockpiles of obsolete pesticides from the African continent, and to put in place preventive measures that will ensure that reformation of stockpiles does not occur. The first phase of ASP covered seven countries: Tanzania, Ethiopia, Mali, Morocco, Nigeria, Tunisia, and South Africa which in total was supported by USD 20,900,000. A second

phase is planned covering 15 additional countries.

The objective of this document is to share the experience gathered during the execution of the first phase of the ASP programme providing inspiration on how to implement such projects and hopefully resulting in exchange of information among the near Eastern and Central Asia project teams and their African counterparts. The document provides country information on the lessons learnt relating to organizational structures established to implement the project; execution approaches; financial aspects as well as observations on the co-operation between the countries and the donors.

SARDAS LANDFILL, HCH MONITORING AND REMEDIATION

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Abstract

From the seventies to the early nineties, the Sardas landfill (Sabiñánigo, Spain) was used to dispose of municipal, construction and industrial wastes. Which were deposited directly onto on Eocene marls without any leachate collection system or bottom liner. The industrial wastes consist of residues derived from the production of chlorine and lindane, including various hexachlorocyclohexane (HCH) isomers. Both in powder and free phase form as Dense Non Aqueous Phase Liquid (DNAPL). This DNAPL is currently seeping as leachate from the landfill to the surrounding area.

Since 2009, the site was investigated and partially remediated by the National and Regional environmental authorities. The jobs completed, consisted in the drilling and construction of more than sixty monitoring and pumping wells: the

environmental characterisation of soil, groundwater, and DNAPL, including the installation of two groundwater pump and treat systems.

The DNAPL flow path is complex and takes place at various levels. After flowing through the waste and seeping through the weathered bedrock base of the landfill, the DNAPL descends to depths of up to 40 metres through fractures in the marls. The main receptor is the River Gállego reservoir. It is located down gradient and is adjacent to the site.

The DNAPL is currently being extracted from pump wells. At the same time, a detailed hydrological survey is being undertaken in nearly all of the existing monitoring points in order to optimize the control of the contamination and environmental risks.

In addition, analyses of dioxins and furans have been completed in samples of soil and groundwater. The results indicate their presence in both of these media. Tests are being conducted to determine the reaction of HCH with the marl substrate and also to verify if an alkaline hydrolysis of the organo-chlorides occurs when interacting with basic leachate.

All these tests and analyses are aimed at to stopping the flow of the DNAPL plume, and, at the same time, to verify the environmental situation of the soil and groundwater, and to increase the knowledge of this site's particular problem. With all of these data, an attempt is made to develop the appropriate corrective actions in the future.

Keywords

Lindane, HCH, marls, landfill, leachate, groundwater, reservoir, DNAPL, Sabinánigo, Spain.

Introduction

The Sardas landfill is situated near the town of Sabinánigo, in the Autonomous Community of Aragón, close to the northern border of Spain with France (Figure 1). This landfill has been used for over two decades, for the uncontrolled disposal of heterogeneous wastes, from both local industries and municipal urban waste.

The total waste volume, is estimated at around 350.000 m³, which includes organ chlorine waste, chlor-alkali wastes, wastes containing heavy metals, oils and hydrocarbons, and urban wastes.

The Sardas landfill is located along a geological ridge structure of folded rock layers. The northern flank of this anticline dips at approximately 30° to the north, while the southern flank is orientated south and is almost vertical. The base of the landfill consists of Eocene marls (Larés marls formation), which is weathered at the surface and fractured in depth.

The industrial and municipal wastes were deposited directly onto the weathered

marls. Without any prior basal impermeabilisation system or a leachate collection system in place. During the period of operation, it is estimated that between 30,000 and 80,000 tonnes of HCH in powder form were deposited into the landfill. Including approximately 2,000 tonnes of liquid waste (DNAPL).

The industrial waste, consists of residues derived from the production (1975-88), of chlorine and lindane including various HCH isomers. Powder form and in free phase form as DNAPL. The latter is currently seeping as leachate.

In the beginning of the nineties, the landfill was abandoned and superficially sealed. Some years later, a road was built through the toe of the landfill. Resulting in the removal of impacted material and deposited, at an unprepared site down gradient and adjacent to the River Gállego Reservoir. One of the consequences of cutting a road, through the landfill, was the necessity for the installation of a slurry retaining wall, both to provide slope stability and to provide a hydraulic barrier to retain the leachate.

The aforementioned reservoir is down gradient to the site, and the water rests upon quaternary alluvial materials. Consisting in silts, sands and gravels which are linked

with reservoir's level. Both the reservoir and alluvial aquifer are the principal receptors of the leachate plume.



Figure 1: Location of Sabinánigo, Spain

Project description

The project included a comprehensive site characterization, necessary to develop a conceptual model of the site. Simultaneously, a provisional remediation system was installed. In order to commence the elimination of the hotspots and to stop the leachate plume reaching the reservoir.

Site characterization

The investigation of the site was funded by the National and Regional environmental authorities. Several companies were contracted to complete the site characterisation, with the objective to develop the site conceptual model, evaluate the environmental situation and apply the best remediation techniques to the site.

An approximate total length of 1,000 metres of ground was drilled in order to install 57 monitoring wells and 12 pumping wells. Two pneumatic pumping plants were installed along with a wastewater treatment system consisting of decantation, physicochemical treatment and activated carbon filtration.

In order to increase the knowledge of the problematic of the site, and also attain the most efficient treatment strategies, diverse investigation techniques have been applied. This included electrical tomography campaigns in the field, laboratory analyses for dioxins and furans, and laboratory tests examining the reaction of organic and basic leachate with the marl substrate. Additionally, laboratory remediation tests have been conducted on waste containing HCH, using per-sulphate, zero-valent iron nano-particles, hydrogen peroxide, etc.

Hydrogeological investigations of the different geological formations have been completed, including pump tests, packer tests in boreholes, periodical field measurements of physical and chemical parameters in piezometres (pH, conductivity and temperature), continuous groundwater level measurements and chemical analyses of groundwater quality, with an extensive range of organic and inorganic parameters. In addition, a hydraulic balance of the landfill has been completed.

Soil, groundwater and DNAPL analytical survey. Since 2009, hundreds of soil and groundwater samples have been collected.

Figure 2. DNAPL composition

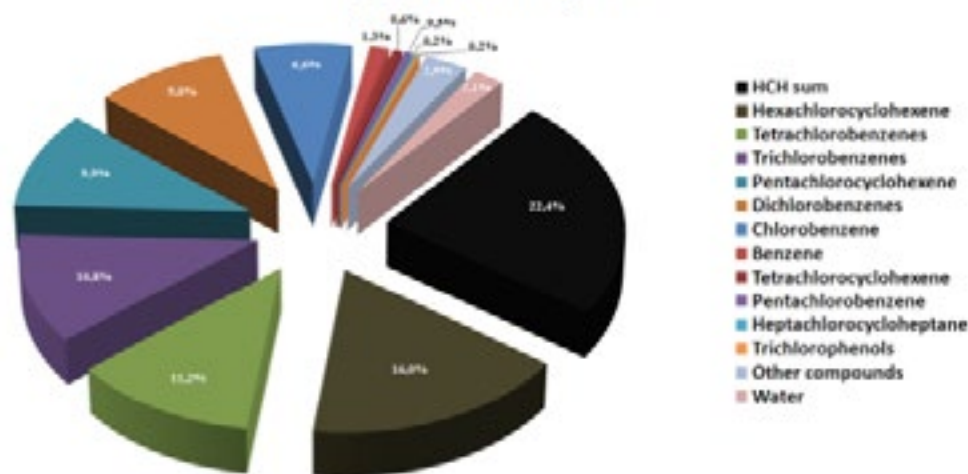


Figure 2: presents the compounds analysed for, including HCH (five isomers).

Table 1 (next page) demonstrated above presents the results of the analyses for dioxins and furans completed on soil samples and fill material. It was obtained from the slope of the road cutting and from the boreholes. Water samples were also collected from the installed piezometers, and from the drainage trench at the foot of the slope where leachate seeping from the landfill accumulates.

Due to the presented results, it is planned to undertake a further study of the dioxins

Table 1. Dioxins and Furans Analytical Results (date April 4th 2013)

Compound	Uds.	Talud PS28	S39DT1	S39DT2	S39DT3	Uds.	LIX-O	LIX-A
		Solid					Liquid	
2,3,7,8-TCDD	ng/kg	>90	<20	<10	>11,000	ng/l	-	-
1,2,3,7,8-PeCDD	ng/kg	>70	17	11	>11,000	ng/l	-	-
1,2,3,4,7,8-HxCDD	ng/kg	>900	430	45	>36,000	ng/l	-	-
1,2,3,6,7,8-HxCDD	ng/kg	>110	700	63	>27,000	ng/l	-	>20
1,2,3,7,8,9-HxCDD	ng/kg	5	210	25	>18,000	ng/l	>600	>20
1,2,3,4,6,7,8-HpCDD	ng/kg	40	680	2,600	>250	ng/l	>900	>10
OCDD	ng/kg	230	2,700	15,000	>300	ng/l	>1,100	>10
2,3,7,8-TCDF	ng/kg	150	150	170	>9,900	ng/l	>1,800	>10
1,2,3,7,8-PeCDF	ng/kg	240	100	210	>900	ng/l	>300	>10
2,3,4,7,8-PeCDF	ng/kg	63	65	220	>2,000	ng/l	>290	>10
1,2,3,4,7,8-HxCDF	ng/kg	31	230	590	>700	ng/l	>190	>10
1,2,3,6,7,8-HxCDF	ng/kg	18	57	200	>170	ng/l	>80	>10
1,2,3,7,8,9-HxCDF	ng/kg	14	5,4	29	>6,000	ng/l	>20	>10
2,3,4,6,7,8-HxCDF	ng/kg	13	20	160	>500	ng/l	>100	>10
1,2,3,4,6,7,8-HpCDF	ng/kg	49	90	410	>250	ng/l	>200	>10
1,2,3,4,7,8,9-HpCDF	ng/kg	8	6,6	180	>230	ng/l	>80	>10
OCDF	ng/kg	-	1,3	240	>290	ng/l	>690	>10
1-PCDD/FTEQ low	ng/kg	290	219	299	60,840	ng/l	24,000	4,700
1-PCDD/FTEQ top	ng/kg	290	239	319	60,840	ng/l	24,000	4,700
WHO-PCDD/FTEQ low	-	-	-	-	-	ng/l	25,000	5,800
WHO-PCDD/FTEQ top	-	-	-	-	-	ng/l	25,000	5,800
Dry matter	%	66.7	79.1	79.4	75.5	%	-	-

and furans. To check if the origins were from the production of HCH, or formed due to consequence of the presence of urban waste in the landfill.

Table 2, represented below, exhibits the elevated concentrations of the organochlorine compounds, especially HCH, both inside the landfill and outside in the area adjacent to the reservoir of Sabiñánigo.

Site remediation

At present, twelve wells are connected to a pumping system for DNAPL extraction. Five points are located on the ridge over-

looking the slope within the landfill and seven are located at the foot of the landfill, down gradient of the slurry retaining wall and road. Periodically, the groundwater from the wells are pumped to 1 m³ storage containers, in which the HCH liquid mixed with water is allowed to decant before it is removed for external waste management (incineration).

The remaining water is then pumped to a specifically designed wastewater treatment plant, including physicochemical and activated carbon treatment before being discharged clean into the reservoir. At the



Figure 3: Settling tank (left) and pumping trench

base of the landfill, a drainage trench with a collection sump, has been installed and a pump periodically extracts the leachate emanating from this zone.

From 2012 to 2013, 0,4 m³ of DNAPL phase and 18 m³ of wastewater has been extracted by the two pumping stations. At the same time, more than 5 x10³ m³ of organic leachate from the surface pump trench has been treated using physico-chemical methods.

The objective of the tests and analyses, were to verify the environmental situation of the soil and groundwater of the site. The results were used to develop, the site conceptual model, and to provide the best solutions to prevent the flow of the plume and if possible, stop its advance.

Table 2. Organic compounds in groundwater (date March 15th 2013)

Date: March 15th 2013	Unit	Piezometer									ST1
		S38-A1	S38B-A1	S38C-A2	PS24-A2	PS24-A3	PS26-A1	PS26-A2	PS26B-A1	PS26B-A2	
Sampling Depth	m	13	27	6	24	30	4	9	26	38	8
Dist. Gállego Reservoir	m	180	180	180	110	110	0	0	0	0	0
Distance to the landfill	m	0	0	0	70	70	180	180	180	180	170
Benzene	µg/l	28,258	25,098	1,935	508	1,583	<0.1	<0.1	<0.1	24.74	596
Chlorobenzene	µg/l	25,861	21,061	4,01	1,378	2,796	<0.1	<0.1	<0.1	2.51	2,705
Dichlorobenzenes	µg/l	8,009	3,550	901	280	406	5.87	9.77	0.36	0.18	2,248
Trichlorobenzenes	µg/l	1,231	685	85	45	39	2.14	2.76	0.18	0.11	541
Tetrachlorobenzene	µg/l	21	18	1.64	1.28	0.65	<0.2	<0.2	<0.2	<0.2	15
Pentachlorobenzene	µg/l	0.37	0.28	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Phenol	µg/l	<0.2	<0.2	35.37	<0.2	33.45	0.76	0.91	0.29	20.51	<0.2
Chlorophenols	µg/l	509	368	25	2.8	3.4	<0.2	<0.2	<0.2	<0.2	0.32
Dichlorophenols	µg/l	98	12	1.51	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
HCH Sum	µg/l	3,763	4,141	414	26	413	12	12	9.53	5.81	481

Site Conceptual Model

The site is complex; however, a brief description of the site conceptual site model is presented as follows (next page):

The knowledge, of the geology and geomorphology of the site, is fundamental in understanding the mechanisms of the flow of the leachate. The landfill, is located on a gully and bounded in by two ridges, and is now covered by the waste. The flow direction of the leachate, will be similar to the flow of water in the gully before it was filled in and covered.

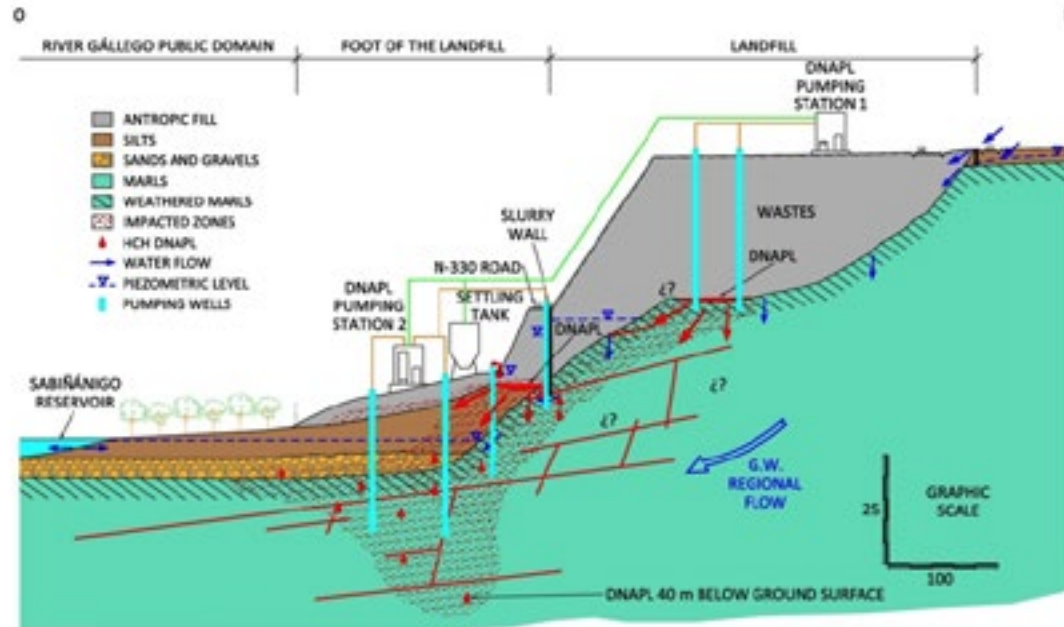
It must be highlighted that the inferior part of the landfill is saturated with a semi steady groundwater level, and it is from here where the leachate seeps into the surrounding area near the slurry wall.

Two principal DNAPL hotspots have been identified, one situated within the landfill and the other-outside, in the proximity of the slurry wall. Both hotspots are on ground possessing low permeability; marls in the base of the landfill, and silt adjacent to the slurry wall.



Figure 4: DNAPL Pumping station 1

Figure 6: Cross section. Conceptual model.



The migration of the plume occurs both in the dissolved phase through the ground-water and as DNAPL. The main transport route of the plume is through the shallow soil levels, and through fill material towards the principal receptor of the Río Gállego Reservoir. At the same time, there is another transport route via the stratification and fractures within the rock substrate where DNAPL has been detected at depths of over 40 metres.

Figure 5: Site layout



The principal receptor is the reservoir of the Río Gállego located adjacent to the site and a connecting quaternary alluvial aquifer existing in the zone.

Conclusions

After four years of the investigation of the Sardas landfill and surrounding area, a conceptual model of the site has been developed. The model indicates that the site poses a major environmental risk to the Río Gállego Reservoir and associated aquifers.

It has been determined that there are two DNAPL hotspots and that the flow route of the plume from landfill, is through fill material, weathered bedrock and through rock fractures within the marls.

57 monitoring wells and 12 pumping wells were installed, the former to control the environmental situation of the site and the latter, to remove HCH waste from the hotspots. Also, a trench has been installed down gradient of the landfill slurry wall and road in order to collect HCH seeping from the toe of the landfill.

The risks to both human health and the ecosystem are still an issue. Currently, the work is progressing, in order to define safe levels and thereby implement appropriate measures to safeguard the environment

and potential impacts on the local population.

Further additional treatment tests are required to assess other alternative potential remediation measures, such as the use of surfactants to help in the extraction of DNAPL, oxidation-reduction processes, etc. Other treatment alternatives will also be reviewed such as in-situ remediation techniques and immobilization or isolation.

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Sardas Landfill, HCH monitoring and remediation



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Introduction

From the seventies to the early nineties, the Sardas landfill (Sabiñánigo, Spain) was used to dispose of municipal, construction and industrial wastes. Which were deposited directly onto an Eocene marls without any leachate collection system or bottom liner. The industrial wastes consists of residues derived from the production of chlorine and lindane including various hexachlorocyclohexane (HCH) isomers. Both in powder and in free phase form as Dense Non Aqueous Phase Liquid (DNAPL). This DNAPL is currently seeping as leachate from the landfill to the surrounding area.

Since 2009, the site was investigated and partially remediated by the National and Regional environmental authorities. The jobs completed, consisted in the drilling and construction of more than sixty monitoring and pumping wells. The environmental characterisation of soil, groundwater, and DNAPL. Including the installation of two groundwater pump and treat systems.

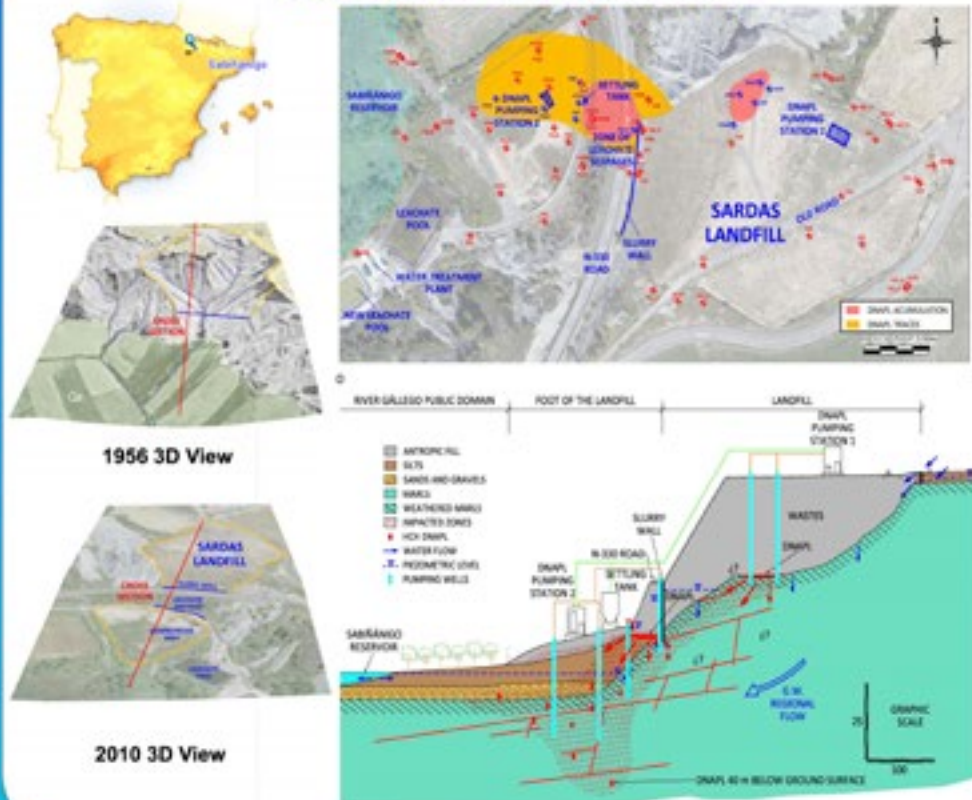
The DNAPL flow path is complex, and takes place at various levels. After flowing through the waste, and seeping through the weathered bedrock base of the landfill. The DNAPL descends to depths of up to 40 metres through fractures in the marls. The main receptor is the River Gállego reservoir. It is located down gradient and adjacent to the site.

The DNAPL is currently being extracted from pump wells. At the same time, a detailed hydrological survey is being undertaken, in nearly all of the existing monitoring points. In order to optimize the control of the contamination and environmental risks.

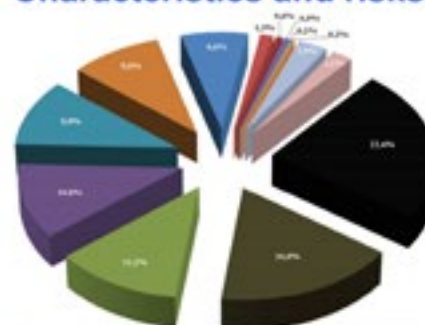
In addition, analyses of dioxins and furans have been completed in samples of soil and groundwater. The results indicate their presence in both these media. Tests are being conducted, to determine the reaction of HCH with the marl substrate, and also to verify if an alkaline hydrolysis, of the organo-chlorides occurs, when interacting with basic leachate.

All of these tests and analysis have the objective to stop the flow of the DNAPL plume. At the same time to verify the environmental situation of the soil and groundwater, and to increase the knowledge of this site's particular problem. With all of this data, try to develop the appropriate corrective actions in the future.

Site layout and cross section



DNAPL Characteristics and risks

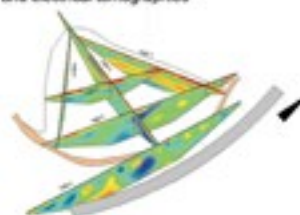


- Hexachlorocyclohexane
- Tetrachlorobenzene
- Trichlorobenzene
- Pentachlorocyclohexane
- Dichlorobenzene
- Chlorobenzene
- Benzene
- Tetrachlorocyclohexane
- Pentachlorobenzene
- Heptachlorocyclohexane
- Trichloroethylene
- Other compounds
- Water

- Complex organochlorine mixture
- Many components are persistent in the environment with a very slow degradation rate
- POPs Persistent Organic Pollutants according to the Stockholm convention
- High density, close to 1.5 g/cm³. The contaminant penetrates to great depth by gravity (detected down to 40 m approx.)
- Bioaccumulative
- Inhalation, ingestion and contact toxicity
- Carcinogenic
- High toxicity to aquatic fauna.
- River Gállego (the main receptor) is adjacent to the site

Site characterization & remedial activities

- 69 Boreholes. More than 1300 meters of total drilling
- 30 Trial pits excavated
- Seismic and electrical tomographies



- Soil, surface & groundwater sampling (hundreds of individual samples)
- Hydrogeological study, including pump tests, packer tests, continuous level measurements and extensive hydrochemical analyses
- Water balance of the landfill
- Laboratory treatment tests with hydrogen peroxide, persulfate and zerovalent iron nano-particles.
- Thermal desorption pilot test
- Laboratory chemical attack tests to check the reaction between DNAPL and the bedrock (marls)
- 2 Pneumatic pumping systems (12 pumping wells)
- DNAPL and contaminated groundwater extraction



- The pumped residues, after decanting, are sent to be incinerated
- Contaminated water treatment (physicochemical and activated carbon treatment)

Site conceptual model

- The landfill does not possess underlining, was placed directly upon the ground surface
- 350,000 m³ of mainly hazardous wastes
- The base of the landfill is water saturated, containing leachate
- The bedrock (marls) is fractured
- The flow of leachate from the landfill is over 3000-5000 m³/yr
- There is a superficial level of weathered marls
- A significant source of DNAPL is located inside the landfill
- There are multiple source of DNAPL downstream of the landfill
- DNAPL was detected at variable depths, from the surface to more than 40 m in depth
- There are two types of leachate: organochlorine and alkaline (pH 12-13)
- River Gállego (main receptor) is close to the site

Further actions

Improvement of the conceptual model of the site

- Further treatment pilot trials and hydrogeological tests
- Additional boreholes and maintaining hydrogeologic controls
- Determination of the vertical component of the deep groundwater flow system
- Investigating the possibility of alkaline hydrolysis or other reactions in the chemical degradation of organochlorines

Maintaining remedial actions

- Increasing the number of DNAPL pumping wells
- Perimeter isolation measures to reduce water ingress into the landfill
- Improvement of the leachate drainage system

Comprehensive risk assessment for human health & ecosystems in order to design a reliable and secure permanent solution for the site

FIELD EXPERIENCE OF POP'S MANAGEMENT IN UKRAINE

I. Marchevsky
CEO, S.I.Group Consort Ltd

The company SI Group Consort Ltd. (Israel) is probably one of the biggest and unique operators of hazardous waste in Eastern Europe.

SI Group Consort Ltd. was established in 2007. The main purpose of establishing exercise was providing activities in several sectors :

- environmental projects : operators are licensed Ukrainian company “ Si Bud Systems LLC “ and “Sigmas Ecology Ltd”, which are having all licenses, resources and experience for hazardous waste operating;

- transportation and logistics services: LLC “ABC Trans” - a licensed transporter having a modern fleet, its own production facilities and transport permits, including international (ADR) for a Dangerous Goods transportation;

The main activity of the company is to implement the integrated environmental programs, including and at the whole state level. And we have succeeded in this.



An integrated approach is to find and develop the best solutions for a specific customer's waste, its placement and complexity of retrieval, and ultimate disposal / destruction of the world by using modern technologies.



Now is practiced by S.I.Group Consort Ltd. the full service hazardous waste management :

- development of technological regulations and instructions in cooperation with the specialized research institutes;
- processing of permits on the international movement of hazardous wastes in close cooperation with states authorities of EU members acc. to Basel convention;
- extraction and repackaging of hazardous waste in certified packaging;
- transportation of the hazardous waste by licensed transport (trucks, vessels, railway)
- destruction / disposal of waste at the facilities of the leading European operators (Veolia, Tredi, Tradebe etc.)
- operations to eliminate the effects of environmental accidents.

All stages, without failure, be approved by the relevant documents that provide the proper level of quality control and transparency in the provision of services. Sure our company is certified according to international standards ISO 14001:2004 and ISO 9001:2008, as well as all subsidiaries

As a National operator for dealing with hazardous waste company S.I. Consort Group Consort, Ltd. with the assistance of its subsidiaries in Ukraine was able to successfully execute the national tasks for the release of Ukraine from residues of hazardous waste left over from the Soviet era.

Some data on the export of hazardous waste from the territory of Ukraine :

2011:

- 10 412 t – obsolete pesticides from all over Ukraine;
- 9 486 t – hazardous waste of HCB (Kalush, Ivano-Frankovsk region);
- 2 351 t – hazardous waste of MNCB-mononitrochlorbenzol (Gorlovka chemical plant, Donetsk region)
- 300 t – hazardous waste of PCB (sovtol oil)

2012:

- 13 061 t - obsolete pesticides from all over Ukraine
- 3 429 t - hazardous waste of HCB (Kalush, Ivano-Frankovsk region)
- 392 t – hazardous waste of MNCB-mononitrochlorbenzol (Gorlovka chemical plant, Donetsk region)
- 272 t – hazardous waste of beryllium (Former military plant “Zapad”, Kiev)

2013:

- 572 t - obsolete pesticides from all over Ukraine
- 441 t – hazardous waste of MNCB-mononitrochlorbenzol (Gorlovka chemical plant, Donetsk region)
- 11 992 t - hazardous waste of HCB (Kalush, Ivano-Frankovsk region)

Total for the period 2011-2013 exported and disposed more than 52 400 t of hazardous waste.

S.I. Consort Group Co, Ltd. offers its services in the implementation of complex programs and large-scale projects at the following way:

- analysis and study of the situation on the spot with the assistance of scientific organizations
- the feasibility study of the project , the technological regulations of work , the development schedule
- execution of works according to customer requirements and legal demands: the collection of hazardous waste , packaging, transportation, disposal / destruction on the respective powers of the European Union
- cleaning and decontamination of the work area , restoration works
- elimination of the consequences of environmental accidents
- monitoring of ecological and sanitary-epidemiological situation in the jobsite
- full documentation of each stage of the works from the moment of loading until the final disposal.

The company specializes in works with large amounts of the special hazardous wastes 1-2 classes, namely organic-chlorine residues (POP's), Mercury contaminated waste, polluted packaging waste, PCB etc.

We have gained unique experiences that allow us to develop solutions with optimal “budget / time” without compromising quality execution.

We are pleased to offer all of our unique experiences and capabilities to achieve the ideal result of our cooperation as well as to find new partners in working with hazardous waste!



OBSOLETE PESTICIDE MANAGEMENT IN ETHIOPIA

H. Shimelis

National Project Coordinator ASP;
Ministry of Agriculture, Addis Ababa, Ethiopia

Ethiopia has a long track record on implementing obsolete pesticides (OPs) disposal projects. In the past, Ethiopia accumulated huge quantities of OPs mainly due to the following factors: inadequate storage and poor stock management; import of unsuitable products; donation or purchase of excess quantities; product bans.

The Ministry of Agriculture (MoA) have since 1996 been engaged in cleaning the country from the OPs stocks and in total 3 projects have been implemented from 2000 up to 2013. 1) Phase-I Obsolete Pesticides Project 1,575 tons of OPs were safeguarded and 1507 tons of OPs disposed of in EU; 2) Phase-II Obsolete Pesticide Project about 1100 tons under two contracts were disposed of in EU and 3) Africa Stockpiles Program (ASP) where Joint Venture “Polyeco-Tredi” has safeguarded over 230 tons and disposed of 450 tons of OPs.

The total project funds for the three projects including repacking, shipment and disposal of about 3,050 tons, capacity building, and project management amounted to a total of 15,000,000 USD. The donors were: The governments of Belgium, Finland, Japan, Netherlands, Sweden, the United States of America; Crop Life International, and Global Environment Facility through the World Bank.

As a result of increased capacity in the country, specifically in the MoA, implementation and execution of projects has changed over the years. The acquired experience has allowed the MoA to undertake more responsibilities in planning and executing the safeguarding operations. In Phase-II obsolete Pesticides Project and the latest ASP Project the MoA staff, with only little assistance from waste management contractors and appointed Technical Advisor, have repacked/safeguarded and collected over 1,300 tons of OP from 800 stores, distributed throughout the country. This considerably reduced project costs by

substituting international hazardous waste management contractors and ensured the swift completion of the projects.

TOX-CARE PROJECT IN CENTRAL ASIA MANAGEMENT OF HAZARDOUS SUBSTANCES AND GOODS

**A SUB-REGIONAL PROJECT FOR CENTRAL ASIAN COUNTRIES:
CONSULTING, TRAINING AND DEMONSTRATION-PROJECTS**

Project Background

The University of applied Sciences North-western Switzerland together with the Regional Environmental Centre of Central Asia (CAREC) launched in 2004 the implementation of the regional project “ToxCare” related to the management of hazardous substances and goods. The project is financed by the Swiss Government, Federal Office for Environment, as part of its efforts to foster cooperation and environmental protection within the GEF Constituency that unites Azerbaijan, Kazakhstan, the Kyrgyz Republic, Switzerland, Tajikistan, Turkmenistan, and Uzbekistan.

The project is aimed at supporting Central Asian countries in their effort to build national as well as local capacities in the area of management of hazardous substances, materials and wastes and is expected to lead to an increase of investments in the waste management sector in Central Asian countries.



Landfill site in Bishkek, Kyrgyz Republic



PCB – containing condenser storage in Tajikistan

B. Fokke
Tauw, Nederland

J. Vijgen
IHPA

M. Jutz
Institute for Ecopreneurship, Switzerland

Objectives and Methodology

The primary objective of the project is to increase the knowledge and expertise of country representatives from the Central Asian region in the area of management of hazardous substances, materials and wastes. The project includes two major components: (1) the training program in the area of management of hazardous waste and chemical substances, and (2) implementation of pilot projects in cooperation with organizations (industries, municipalities and institutions) interested in the development of hazardous waste management systems and/or in implementation of a technical project on the handling of hazardous substances and goods.

Obsolete pesticides
management in Tajikistan:
mission 2012

In 2009 the ToxCare project organised a workshop in Dushanbe on Persistent Organic Pollutants (POP's) and obsolete and

POP's pesticides and PCB management. In parallel TAUW (NL) and its consortium partners IHPA (DK), Witteveen+Bos (NL) and Milieukontakt (NL) analysed with the support of the World Bank the situation of the contamination through POP and obsolete pesticides in the southern part of Tajikistan. As there was one major remaining obsolete and POP's pesticides contaminated site in the northern part of Tajikistan, close to Kanibadam, to be analysed, it was decided to organise a common mission to this place in 2012.

The major objectives of the mission were:

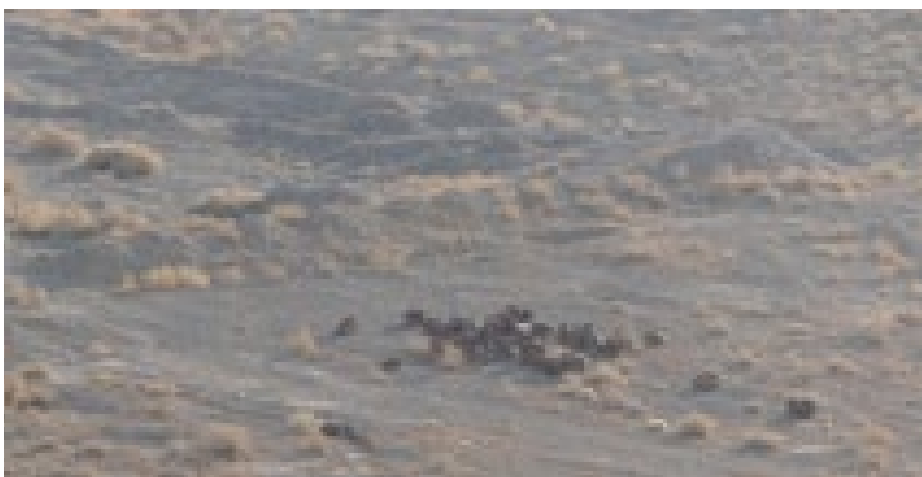
1. A five day training for eight local experts in contaminated site assessment, risk assessment and burial site management at the obsolete and POP's pesticides landfill Kanibadam
2. Presenting in a national workshop in Dushanbe the outcomes of the risk assessment in Kanibadam and developing a national implementation strategy in accordance with the National Implementation Plan (NIP) for the Stockholm Convention on POP's in Tajikistan.

The mission was planned and executed in a joint project with the following partners:

- University of Applied Sciences Northwestern Switzerland, Prof. Maurice Jutz, (lead)
- IHPA (DK), Mr John Vijgen, TAUW (NL), Mr. Boudewijn Fokke, Witteveen+Bos (NL), Mr Maarten van der Wijk and Ms Ingrid van der Rijk
- Committee for Environment Protection under the Government of the Republic of Tajikistan, Mr Salimov, Talbak, Chairman
- FSCI, Chair of Public Association "Foundation to support civil initiatives" (TJ), Ms Muazama Burkhanova, PhD (lead local organisation and project support)

Kanibadam POP and obsolete pesticides Polygon: history
During the Soviet Era huge quantities of pesticides were imported to Tajikistan and bordering countries to be used by the community farmers. The main crop was raw cotton. The problem dates back to the 1950s and 1960s, when the import and use of pesticides, in what were then Communist countries, was increased in order to raise agricultural production. Pesticides were distributed to farmers nearly free of charge, leading not only to overuse, but also to unsound management of residuals

and packaging materials. The assortment of used pesticides included chemicals which later were included in the POPs-list of the Stockholm Convention such as: Aldrin, Dieldrin, Heptachlor, Endrin, Hexachlorobenzene, Toxaphene and DDT. These plant protection chemicals accumulated in the environmental components of the densely populated, irrigated territories of the Republic of Tajikistan and became serious sources of concern. Therefore also the Soviet banned the use of obsolete and POP's pesticides and constructed all over their territories polygons with sarcophagi to permanently store the banned pesticides. After the collapse of the Soviet Union these well-guarded and maintained polygons were left orphaned. These polygons were and are opened (waste mined) by mostly young men to sell these pesticides to poor farmers. Poor farmers use these as alternative for the officially approved expensive pesticides. These waste miners are exposed to toxic waste and have ruined these sites resulting in an enhanced dispersion of these toxic chemicals in the surrounding environment. Nowadays the environmental challenges caused by these past actions, may contribute to serious health and environmental pollution risks in Central Asia. Pesticide diffusion to the environment knows no borders and gi-



Overview of the Kanibadam polygon

ven the transnational nature of this issue, the governments of Kyrgyzstan, Uzbekistan and Tajikistan need to cooperate and coordinate on their environmental security together to find best solutions.

Kanibadam polygon is located in Sugd region in 7 km from Kanibadam city in southeast direction. Territory of this polygon is about two hectares. About 9,000 tons of POP and obsolete pesticides have been buried on the site in the past. The relief of this territory is hilly with a dendritic drainage pattern. The drainage gullies are most of the year dry. The surface of the hill-

ocks and slopes are stony (dessert pavement) due to wind erosion of the finer soil particles. The soil texture is silty / clayish till at least up to 30 meter. The soil has a low permeability. Therefore most of the rainwater is drained by runoff causing the all kind of soil erosion. The groundwater at the polygon is deeper than 30 meters minus surface.

The territory of this polygon is located hypsometrically, 275 meter higher then Kanibadam city with the inclination of relief to the city, where there are two main canals and seven groundwater wells of various purposes. Availability of dry ditches, two of which have their roots in the burial places, stipulates in great extent the flowing of sediments. From geological point of view the site contains mudstone stream sediments with pebbles, boulders and gravel. Such layer is characterized by high penetrability for precipitations with components of various substances, including obsolete and POP's pesticides.

Activities under the mission 2012

The mission of 2012 was carried out to:

- Assess the Kanibadam polygon together with the stakeholders in Kanibadam to:

- Build awareness of the environmental site conditions and its impact
- Build capacity on the site assessment and environmental sound site management

- Share the site assessment results with the decision makers in Dushanbe to:

- Build awareness of the environmental site conditions and its impact
- Create a sense of urgency to act now to improve the environmental conditions
- To discuss to short term simple measures eliminating the direct risks

The expected results are to:

- Gain a better understanding understanding of the understanding of the



Group session on making a Conceptual site model



Instruction using Personal Protective Equipment
Kanibadam site conditions

- Identify knowledge gaps to design short term mitigation measures addressing the direct risks
- Raise the awareness that fencing, run-off control etc. are simple and effective environmental risk reducing measures
- Create a steppingstone for the local and national agencies to turn these sinks in sites that are maintained and controlled as long as there is no means available for final disposal of the obsolete and POP's pesticides.

Site assessment training

The training was a theoretical and practical training in site assessment. The four

following phases of environmental sound site management were discussed:

- Phase 1 Preliminary site assessment
- Phase 2 Site assessment
- Phase 3 Site management
- Phase 4 Site monitoring and aftercare

Site assessment results

Nowadays, the environmental condition of the Kanibadam polygon is extremely bad. Due to lack of fencing and guarding (site management) sarcophagi are waste mined and chemicals migrate off site. Trespassers (mostly children) with cattle, flora and fauna are exposed to toxic waste.

At the Kanibadam site buried pesticides are manually mined and using backhoe. All over the territory empty metallic and plastic containers can be found. The scattering of obsolete and POP's pesticides, leading to the soil contamination of polygon territory, is observed. High temperature during summer periods and intensive solar radiation contribute to decomposition of pesticides. Frequently recurring local winds and windstorms contribute to transmission of harmful substances and objectionable odour from the burial place to great distances. This Kanibadam polygon is seen as an environmental hotspot. It is a leaking sinks.

Erosion control measures such as terraces, a sluice, built in former time in this polygon for reducing run off; collecting rain and controlling gully erosion are destroyed. The soil erosion processes contribute to the contamination of low territories with obsolete and POP's pesticides.

Various soil samples are taken for chemical analyses and the fieldwork results and chemical analytical results are used to update the Conceptual Site Model (CSM). With the CSM the knowledge gaps for designing short term mitigations measures reducing the direct risk are identified. These results are reported in a Kanibadam site assessment report of Witteveen+Bos and Tauw.

Workshop in Dushanbe

The two day workshop was held in Dushanbe to give the representatives of the relevant ministries and the staff of the Vashkh polygon the opportunity to participate. The workshop started on October 29 and was closed the day after.

The results of the Kanibadam training were presented by trainees. The status of the implementation of NIP on the POP pesticides Stockholm Convention was shared by Ms. Bobritskaya Ludmila Sergeevna. Gaps and hurdles for site reha-



On-site training with PPE



Soil sampling

bilitation were inventoried in group sessions and plenary discussed. The overall conclusion was that implementation of the necessary measures elaborated in the NIP and mentioned in the World Bank report came to a standstill because the whole package of mitigation measures reported



Hotspot sampling



Certification ceremony

in the World Bank report is as a whole financially not feasible for Tajikistan to implement under the current financial regime of the World Bank.

The outcome of the discussion was used to write a road map with the focus on simple and effective short term measures from the above mentioned package addressing the direct risks.

The final result of the workshop is a resolution conveying the message that immediate appropriated short term measures reducing the direct environmental risks due to the obsolete and POP's pesticides should be taken for the:

- Polygon in Vashkh and Kanibadam
- Former community farms with buried stocks obsolete and POP's pesticides
- Sites with remnants of stocks of obsolete and POP's pesticides

Immediate actions to be taken
The outcomes of the risk-assessment during the ToxCare mission in 2012 are

summarised in an action list attached to the above mentioned resolution. These actions should be implemented as soon as possible in order to protect the local population and environment from further negative impacts of emissions of the polygons and other obsolete and POP's pesticides

contaminated sites. The proposed short term actions are simple and can be implemented with local available material and are not costly. Examples of these measures are:

- Reinstall site management
- Install proper fencing and warning signs
- Inform local population about the danger of
 - Using obsolete and POP's pesticides
 - Entering the POP and obsolete pesticides contaminated sites
- Create local commitment and engagement in order to create sustainability by establishing local owner-ship by:
- Implementing construction measures with local craftsmen and workers
- Establishing a local defence organisation that will take care of construction works implemented and take access control and guards
- Prohibit cattle breeding in the surroundings

Because of the low precipitation and the deep groundwater level the workshop participants are confident, that these simple actions can be effective. But express that the other necessary mitigation measures are still to be prepared and planned while the short term measures are containing the site.

The remaining mid-term mitigation measures are:

1. Monitor migration of the pollution to be aware of the effects of the short term measures
2. Capping the polygon preventing infiltration of rainwater and migration of contaminants to deeper soil layers and finally to the groundwater

3. Implement soil erosion control measures preventing off site migration of contaminants

The remaining long term mitigation measures are:

1. Repack and dispose all the POP and obsolete pesticides
 2. Remediate the contaminated soil
-



HEALTH PROBLEMS AT OBSOLETE PESTICIDES SITES (EXPOSURE AND TOXICITY OF PESTICIDES)



PREVALENCE AND RISK FACTORS FOR LIVER DISEASE IN THE SANTOS AND SÃO VICENTE ESTUARY

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Abstract

The Santos and São Vicente Estuary suffers from contamination by toxic industrial waste that has affected the local population health. This study aims to evaluate the prevalence of liver disease in the Santos and São Vicente Estuary, alongside possible risk factors. A cross-sectional study was conducted in four contaminated estuary areas (Pilões and Água Fria, Cubatão Center, São Vicente, Guarujá) and in an outside Estuary area (Bertioga). A questionnaire that addressed socioeconomic conditions, occupational exposure, alcoholism, and morbidity was applied in 820 households in each area. The prevalence of liver disease, hepatitis, cirrhosis and liver, biliary tract or pancreas cancer was calculated. The associations between the

outcome prevalence and the areas were calculated using the Chi-square test, Fisher's exact test or the Difference between two proportions test. Univariate and multiple logistic regression models for the analysis of the risk factors were applied. The significance level for all analyses was 5%. Hepatitis prevalence among all participants was higher at Pilões and Água Fria (1,2%). Among the individuals who reported having liver disease, hepatitis was the most frequently mentioned disorder, and there was a statistically significant association between residence in Pilões and Água Fria and hepatitis presentation (Pearson χ^2 : $z=18.1$; $p<0.05$). 13% to 49% of people who reported having liver disease did not report exposure of any kind.

Occupational exposure to chemicals, alcohol consumption, consumption of locally produced milk (OR=2.88; CI95%:1.24 – 6.70) and fruit (OR=2.43; CI95%:1.13 – 5.23) and water from natural sources (OR=4.44; CI95%:1.73 – 11.40) appeared as risk factors for liver disease. Thus, the contamination of the environment at Santos and São Vicente estuary is still a public health concern.

Keywords

Cross sectional study, environmental contamination, liver disease, hepatitis, cirrhosis.

Introduction

The Santos and São Vicente Estuary, located in the southern coast of the state of São Paulo, suffers from contamination by toxic industrial waste, which has polluted natural resources and affected the health of the local population (Santos Filho et al, 1993; Silva, 1998; CETESB, 2001; Luiz-Silva et al, 2002; Santos Filho et al, 2003; Zago et al, 2005; Oliveira et al, 2007). However, there is still much to be researched regarding the magnitude of the problem and the potential health effects that may result from exposure to these toxic substances. Therefore, this study aims to evaluate the prevalence of liver disease in the region of the Santos and São Vicente Estuary, alongside possible risk factors.

Methodology

A cross-sectional study was conducted in four areas of the estuary, located near or on industrial waste areas: Pilões and Água Fria (area 1), Cubatão Center (area 2), São Vicente Continental (area 3) and Guarujá (area 4), and in one area outside the estuary: Bertioga (area 5), a control area, with no history of contamination. Figure 1 shows the five selected areas.

The data collection instrument was a questionnaire that addressed socioeconomic conditions, infrastructure, demographics, occupational exposure, alcoholism, smoking and morbidity. The questionnaire was based on the questionnaire developed by the National Cancer Institute (INCA in Portuguese) entitled “The Household Survey on Risk Behaviors and Morbidity Referred of Non-communicable Disease” (INCA 2003) and adapted for this study’s

aims. Eight hundred and twenty households in each area were randomly selected. In order to be considered a liver disease case, an individual being interviewed had to present any of the following documents: a letter from a physician attesting the presence of the disease; a recent prescription of medicine for liver disease; or any other document from the Labor Court confirming the presence of any liver disease. The questionnaire was pre-tested in one of the



Figure 1: Studied areas: located in and outside the Santos and São Vicente Estuary

estuarine areas, and relevant adjustments were implemented before its use in the main study. A term of free and informed consent for each interviewed household was filled out. The study was approved by the Ethics Committee of the Hospital das Clínicas, Faculty of Medicine, University of São Paulo (Research Protocol No. 350/07).

The prevalence of liver disease, hepatitis, cirrhosis and liver, biliary tract or pancreas cancer was calculated. The associations between the prevalence of the outcomes of interest and the areas were calculated using the Chi-square test (incorporating the Yates correction for continuity), Fisher's exact test or the Difference between two proportions test and univariate and multiple logistic regression models for the analysis of the risk factors. The significance level for all analyses was 5%, and the analyses were performed using the Statistical Package for Social Sciences (SPSS) 15.0 for Windows.

Results

There was no statistically significant association between the presentation of liver disease and residency in the studied areas ($p = 0.13$). However, the prevalence of this disease in Cubatão Center was higher and statistically different from the prevalence

observed in Guarujá (comparison between two proportions test $z = 2.16$, $p = 0.03$).

In the no-exposure sample, the prevalence of liver disease at São Vicente Continental was higher and statistically different from the prevalence observed in Guarujá (comparison between two proportions test $p = 0.02$). The prevalence of hepatitis among all participants was higher in Pilões and Água Fria (1,2%). Among the participants who reported having liver disease, hepatitis was the most frequently mentioned

disorder, and there was a statistically significant association between residence in Pilões and Água Fria and hepatitis presentation (Pearson χ^2 : $z = 18.1$, $p < 0.05$). People presenting other liver disease (48.7%), cirrhosis (13.3%) and hepatitis (27.7%) did not report exposure of any kind.

Figure 2 shows the prevalence of participants that mentioned having some kind of the studied liver disease and exposure to

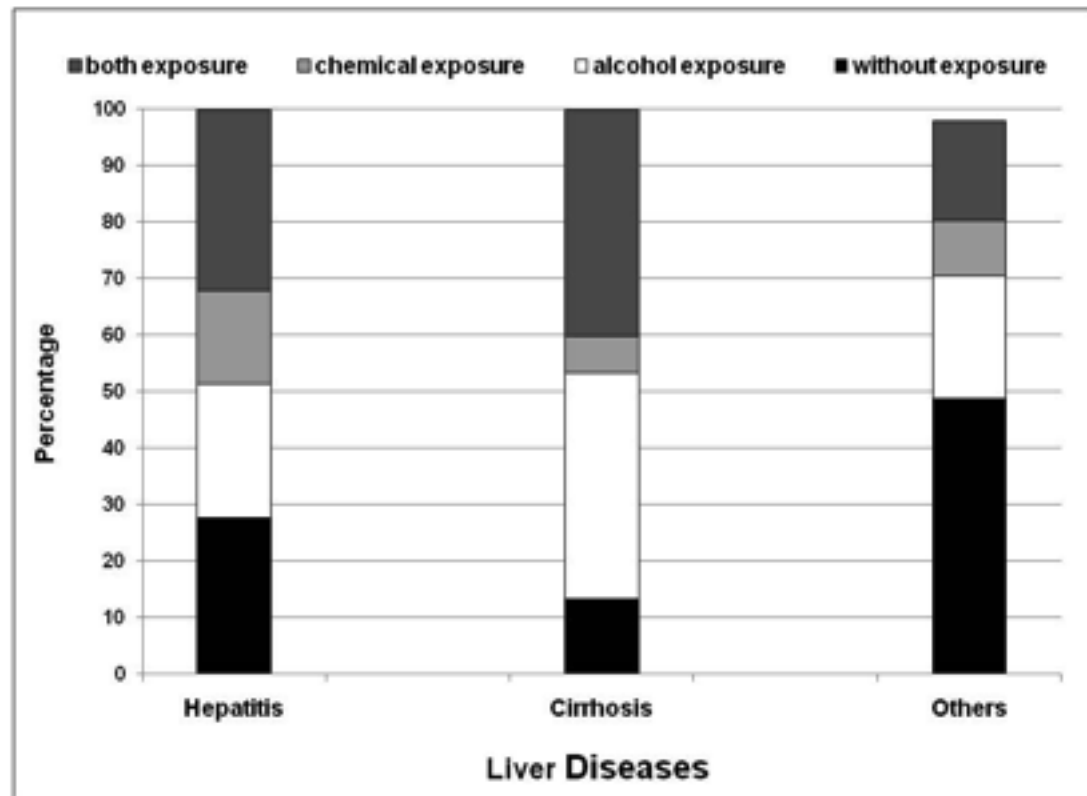


Figure 2: Prevalence of participants that mentioned having some kind of the studied liver disease and exposure to alcohol and chemical substances

Table 1 shows the risk factors that, in this study, were shown to be occupational exposure to chemicals, alcohol consumption, the consumption of locally produced milk and fruit and water consumption from natural sources.

Table 1. Results of single logistic regression and multiple logistic regression models.

		Single model	Multiple model
		OR (CI 95%)	OR (CI 95%)
Liver disease	Occupational exposure to chemicals	2.50 (1.78 – 3.49)*	1.90 (1.29 – 2.80)*
	Alcohol consumption	2.08 (1.56 – 2.79)*	1.62 (1.10 – 2.37)*
	Local fruit consumption	2.43 (1.13 – 5.23)*	3.13 (1.12 – 8.19)*
	Local milk consumption	1.87 (1.10 – 3.17)*	1.51 (0.64 – 3.59)
Hepatitis	Occupational exposure to chemicals	3.22 (2.07 – 5.02)*	2.69 (1.62 – 4.47)*
	Alcohol consumption	1.94 (1.31 – 2.90)*	1,55 (0,93 – 2,57)
	Local fruit consumption	3.91 (1.70 – 8.99)*	4.58 (1.60 – 13.13)*
Cirrhosis	Occupational exposure to chemicals	3.40 (1.23 – 9.40)*	1.52 (0.53 – 4.35)
	Alcohol consumption	5.87 (2.13 – 16.17)*	6.22 (1.68 – 22.98)*
Others liver disease	Local milk consumption	3.44 (1.71 – 6.94)*	_____

Liver disease (without occupational exposure)	Alcohol consumption	1.84 (1.16 – 2.92)*	1.82 (1.14 – 2.90)*
	Local milk consumption	2.88 (1.24 – 6.70)*	2.52 (0.99 – 6.40)
Hepatitis (without occupational exposure)	Alcohol consumption	2.17 (1.13 – 4.16)*	2.07 (1.08 – 3.97)*
	Natural local water consumption	4.44 (1.73 – 11.40)*	5.88 (2.24 – 15.45)*
Cirrhosis (without occupational exposure)	Alcohol consumption	7.72 (1.56 – 38.30)*	_____
Other liver disease (without occupational exposure)	Local milk consumption	4.86 (1.70 – 13.90)*	_____

*statistically significant

Discussion

The prevalence of total liver disease among all participants was low, but hepatitis was the most frequently mentioned disorder. The prevalence of hepatitis, among all participants, of Pilões and Água Fria, Cubatão Center and Continental São Vicente were higher than the prevalences at Guarujá and Bertioga. However, about one third of the people who mentioned having hepatitis and almost half the people who mentioned having other liver disease reported not being exposed to chemical and alcohol consumption. The consumption of locally-produced food may serve as route for exposure to environmental contami-

nants. However, almost all interviewed households (97.0%) in the present study reported that they did not consume food produced in their communities, and the consumption of local milk. Fruit and local sources water appeared as risk factors for liver disease and hepatitis, as did occupational exposure to chemicals and alcohol consumption.

The adoption of a cross-sectional design seemed to be the best choice to explore the effect indicators of the environmental exposure to chemicals in the Santos and São Vicente Estuary. Despite the well-known histories of area contamination and inhabitant exposure throughout the last four de-

CADES, complete contamination routes are not well-defined and there is also concern regarding the ability of public health services to identify and treat cases of disease related to exposure to environmental contaminants.

Conclusions

The contamination of the environment at the Santos and São Vicente estuary is still a public health problem, and it is still necessary to consider the limitations of the health system in identifying and diagnosing all cases of environmental exposure to different contaminants as risk factors for the presence of disease.

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EFFECT-BASED ASSESSMENT OF PERSISTENT ENVIRONMENTAL POLLUTANTS USING MAMMALIAN REPORTER ASSAYS

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Abstract

Environmental risk assessments based on chemical analysis combined with hazard based equivalency factors are limited by the relatively small set of contaminants that are routinely included in environmental screening programs, as well as by the limited toxicological knowledge that is available for the vast majority of compounds. This drawback may be obviated by including a complementary assessment approach that focuses on biological effects of compounds cocktails rather than on chemical analysis of the presence of individual compounds. This can be achieved by the use of reporter assays that respond to specific biological effects, such as CALUX assays. These assays are based on human cell lines that were modified to respond specifically and quantitatively to compounds that impose a certain effect on the cells. There are over 25 CALUX assays available, including

assays for endocrine disruption, dioxin receptor-mediated signaling, endpoints that relate to genotoxicity and carcinogenicity, and multiple stress pathways. Due to its standardized set up, it allows for reproducible high throughput measurements. The assays are used for a wide variety of applications, among which effect-profiling of pure compounds, hazard assessment of complex (environmental) mixtures, and screening of human tissue in epidemiological studies.

Keywords

POPs, Pesticides, CALUX, reporter assays, effect-based assessment.

Introduction

From the millions of chemical compounds produced by man, a substantial part ends up in the environment. In general, envi-

ronmental hazard assessments focus on chemical analysis by measuring only a limited set of prioritized compounds for the reason that they frequently occur and/or are known to provoke adverse health effects. Although, in many cases, this chemistry-based approach may give a representative impression of the toxicological hazards of a sample, this approach will not identify hazard by compounds that are not included in the screening program. However, simply including more compounds does not solve this problem, as most compounds have not been thoroughly tested for their in vivo effects. In addition, chemical analysis cannot assess the possible interactive behavior of compounds in mixtures.

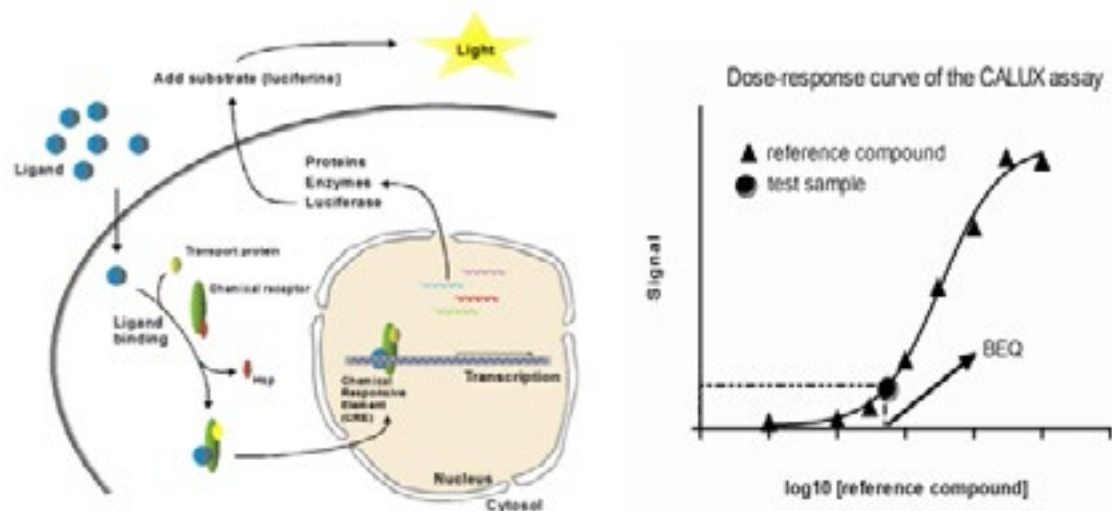
These flaws may be overcome by including effect-based testing, i.e. direct assessment of adverse effects without the requirement of prior knowledge of the

sample composition. Toxicological hazard assessment of pure compounds is generally done by animal testing. Obviously, ethical issues related to animal testing, high cost, variability in the constituents of the sample and amount of time required for analysis, disqualify this approach for standard applications in environmental screening programs.

An alternative approach is effect-based hazard assessment, i.e. by the use of in vitro assays, which rely on cells derived from relevant vertebrate species. These tests focus on distinct effects on the tissue or cellular level that play an important role in the onset of major toxic effects at the organism level (such as carcinogenicity, genotoxicity, reproduction toxicity and developmental toxicity).

CALUX reporter assay principle

The CALUX panel is a set of human cell line-based reporter assays that were modified to generate a very specific and dose dependent response to compounds or mixtures that impose a certain effect. These cells produce light upon exposure to samples that impose the effect of interest, and the amount of light produced is proportional to the amount of specific biological



The CALUX consist of mammalian cells that were modified to respond specifically to a certain effect by the production of an enzyme, luciferase (left). Cells are exposed to a test sample along with a concentration series of a reference compound. After an exposure period, the substrate is added for the luciferase, after which light production is quantified on a luminometer. The final result is expressed as biological reference compound equivalences (BEQ), by interpolation in the dose-response curve of the reference compound (right).

activity in the sample. The effect is expressed relative to the effect of a well-defined reference compound (see box).

Relation of CALUX assays with in vivo toxicity

Currently, over 25 CALUX assays are available that are predictive for various toxic effects at the cellular level. These cellular effects were targeted for their

relation with major toxic events in vertebrate species. Some examples of how the in vitro assay data relate to in vivo effects are listed below:

- The AhR receptor, which binds dioxins, dioxin-like PCBs and various PAHs, has a pivotal role in the initiation of dioxin related toxicity (Marlowe and Puga, 2005) and in detoxification processes. The central role for AhR was confirmed in studies

with mice, in which AhR-knockout resulted in reduction of toxic effects by dioxin and PAHs (Gonzalez and Fernandez-Salguero, 1998; Nakatsuru et al., 2004; Shimizu et al., 2000). The AhR-based DR CALUX is optimized for the detection of dioxins and dioxin-like PCBs. The related PAH CALUX cell line is sensitive for especially those PAHs that have been indicated as mammalian carcinogens (Pieterse et al., 2013);

- Disruption of the endocrine system can result in multiple adverse effects, including reproduction and developmental disorders and various cancers. CALUX assays are available for the detection of interference of cellular processes via a range of endocrine receptors, including the Estrogen Receptor alpha (ER α), the Estrogen Receptor beta (ER β), the Androgen Receptor (AR), the Progesterone Receptor (PR), the Glucocorticoid Receptor (GR), the Retinoic Acid Receptor (RAR) and the Thyroid Receptor beta (TR β). These assays were validated by screening of model compounds. Moreover, the predictive value of the ER α CALUX, the AR CALUX and the PR CALUX for in vivo effects was confirmed in studies that showed good correlations of the assays with analogous in vivo models (Sonneveld et al. 2006; Sonneveld et al., 2011);

- Peroxisome proliferator-activated receptors (PPARs) are major regulators involved in lipid and glucose metabolism, which also relates them to chronic disorders such as obesity, and obesity-induced inflammation and diabetes. Currently CALUX assays for PPAR α , PPAR γ , and PPAR δ are available;

- P53 is the major regulator for cell cycle arrest, activation of DNA repair mechanisms, and initiation of apoptosis in response to DNA damage, processes that directly relate to genotoxicity. Mutations that disrupt the functionality of the p53 gene lead to uncontrolled cell growth and, thus, cancer. Validity of the p53 CALUX as predictor of genotoxic action has been confirmed in a validation study using a reference set of test compounds proposed by the European Union Reference Laboratory for alternatives to animal testing (EURL ECVAM) (Van der Linden et al., 2013).

Effect-profiling of pure compounds
The CALUX panel has been used for the generation of in vitro effect profiles for an extensive set of persistent environmental pollutants. These effect profiles provide information on the potency of the compound with respect to a large number of toxicity endpoints. Moreover, they could

provide an indication for the type and level of pollution that is present in field samples, for which profiles of the total mixture have been generated. Despite the heterogeneity of the responses towards the various compounds, dominant effects could be observed: Major part of the tested pesticides interacted with major hormone receptors, particularly anti-androgenic, anti-progestagenic and /or estrogenic were observed. It was previously stated that endocrine disruption is a dominant effect of many pesticides, which may be linked to known adverse health effects, such as carcinogenicity and developmental disorders (Mostafalou and Abdollahi, 2013). Most of the pesticides that have been associated with carcinogenicity do not have an effect on the p53 CALUX, which indicates a non-genotoxic carcinogenic mode of action. Dioxins, dioxin-like PCBs and carcinogenic PAHs are characterized by their inducing effect of AhR-mediated activity. The effects evoked by the heavy metals and the organometals confirm that they are very diverse with respect to their toxic effect. From the screened compounds, 14 compounds showed a response in the p53 CALUX assay indicative of genotoxic effects. Genotoxicity is confirmed in scientific literature for 11 of these compounds.

Applications

The CALUX assays are effect-based biological measurement techniques, for which the use is not restricted to specific matrices or research areas. Analyses are done for food and feed compliance testing, environmental quality testing, effect profiling of pure compounds, and screening of human tissue, for instance, in epidemiological studies. The assays have been used in research projects worldwide. We provide some illustrative examples of projects that relate to environmental safety.

Soil and sediment

The DR CALUX is frequently used as sensitive and cost-effective alternative for the assessment of dioxins and dioxin-like PCBs in soils and sediments. This approach is approved by regulatory agencies in multiple countries.

While PAHs form one of the most widespread and heterogenic group of environmental pollutants, screenings are generally restricted to one or a few prioritized congeners. The PAH CALUX offers an alternative approach by quantification of the AhR-mediated activity of the total PAH mixture. This appears to be a strong indicator for the abundance of carcinogenic PAHs (Pieterse et al., 2013). The comparison of PAH CALUX measurements with chemical analytical data of river sediment,

sewage sludge and industrial soil showed that application of this bioassay reduces the risk of underestimating the actual toxicity as compared to the exclusive use of chemical analytical data.

In a project on the hazard assessment of a pesticide dump site in Tajikistan, a combined approach using chemical analysis and a set of CALUX reporter assays was used (Rijk et al., 2013). CALUX-based bioactivity profiles specifically indicated the high endocrine disrupting activities at the hotspots. Comparison of the bioassay data with chemical analytical data showed that the analysed compounds could only account for a part of the total biological activity.

Water

CALUX assays are frequently used in water quality assessments for the detection of endocrine activity. The main emphasis is put on the presence of estrogenic activity, which is frequently detected in many water systems worldwide and has been shown to have devastating environmental effects at even ng/l concentrations (Kidd et al., 2007). Based on the biological activity detected, many responsible compounds have been identified chemically, including synthetic hormones and industrial chemicals (Campbell et al., 2006). Recently, other types of endocrine activity in wa-

ter samples have gained more attention, including activity on the glucocorticoid receptor by pharmaceuticals (Van der Linden et al., 2008).

Indoor environment

Indoor dust is a sink for a highly heterogeneous set of pollutants, such as flame retardants and plasticizers originating from household items. A study in which effect-profiles of household dust and various flame retardants were compared showed interactions with hormone receptor for multiple compounds and revealed several candidate high-priority endpoints and compounds for the monitoring of indoor environment (Suzuki et al., 2013).

Wildlife

Several studies have been aimed at the detection of biological activity in wildlife, to assess the effects of exposure to anthropogenic compounds. Recently, in a study on bioaccumulative pollutants in liver and / or blubber extracts from high-trophic animals from Baikal Lake dioxin-like and anti-androgenic activities were identified, while no activities were measured in the estrogen-, progesterone- and glucocorticoid receptor CALUX'. In a combined bioassay – chemical analysis approach, p,p'-DDE was identified as major contributor to the anti-androgenic activity (Suzuki et al., 2011).

Screening of human samples

CALUX-based analyses have been performed on serum, breast milk, and urine samples, as well as on tumour material. Within the European NewGeneris project, maternal and cord blood samples from over 1000 mother – newborn cohorts have been analysed for estrogenic-, androgenic- and dioxin-like activities. One of the major advantages of the bioassays was their high sensitivity, due to which only small sample volumes were required. The results gave strong indication of a relation between dioxin levels and aberrant anogenital distances among male newborns (Papadopoulou et al., 2013; Pedersen et al., 2010).

Future perspectives

The strong potential of effect-based testing using in vitro assays is gaining increased attention, not only by the scientific community but also by regulatory authorities. To illustrate, in a recent EU report, it was stated that the current knowledge gap with respect to mixture toxicity should be bridged in respect of the principle of reducing tests with vertebrate animals (European Union, 2012). Moreover, various initiatives that will promote further use of in vitro methods in the near future are ongoing, such as the ToxCast and Tox21 programs by the US-Environmental Protection Agency, the establishment of the European Union Reference Laboratory for alternatives to animal testing

(EURL ECVAM) in 2011, and the establishment of multiple research consortia that focus on the development of alternative toxicity testing strategies for several adverse health effects (such as the EU FP7 program ChemScreen).

Whereas regulatory guidelines for environmental health quality typically rely on threshold concentrations for prioritized compounds, environmental quality standards can also be set for effect-based data. For the detection of dioxins and dioxin-like PCBs, biological equivalence values are available and acknowledged for various matrices, such as food, soil and sediment. Recently, the Dutch KWR Watercycle Research Institute proposed trigger values for endocrine activities in drinking water based on the ER α -, AR, PR-, and GR-CALUX' (Brand et al., 2013).

Recent developments in assay automation and volume downscaling have resulted in a substantial increase in throughput in combination with a decrease in assay volume and thus sample requirement. This further promotes the use of larger effect-based panels for various applications.

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TO REACH OR NOT TO REACH OR: INADEQUACIES OF OUR CHEMICAL LEGISLATION

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The over-all defining criteria for inclusion of POP-chemicals (i.e. Persistent Organic Pollutants) in the Stockholm Convention lists will - beyond the general properties of toxicity and eco-toxicity, including persistence and bio-accumulative properties - be the potential for long-range environmental transport.

Unintended presence and generally global, individual distribution of these chemicals in living organisms, including habitats and physical surroundings is exemplified by data from equatorial plains, temperate regions and urban areas to arctic regions (re DDT, PCB, HCB & mercury etc.), often far away from places or geographical zones where the original release into the environment took place and resulting from intentional uses or handling or unintentionally as part of chemicals life cycle, processing or waste handling. While indications are given on a possibly stabilised/only slightly changing situation as for example for atmospheric Dioxins and

chlorinated POPs in the Baltic Sea region, new investigations point to still emerging problems concerned e.g. with fluorinated compounds on the Faeroe Islands and mercury in arctic regions.

As for the legislative process concerned with SVHC-chemicals (Substances of Very High Concern), it is a disturbing fact that the inclusion of individual chemicals into the Convention lists not only is a lengthy process per se. Generally it is also unduly delayed due to legislative inadequacy (cfr. unclearly defined burdens of proof) and/or lack of political will to utilise existing tools. The application of Precautionary Principle as defined thru the EU chemical legislation REACH, is lacking behind, as exemplified by present concerns over EDCs, i.e. Endocrine disrupting Chemicals, such as brominated flame retardants and fluorine household chemicals.

ENDOCRINE ACTIONS OF PESTICIDES IN THE FLEMISH ENVIRONMENT AND HEALTH STUDIES

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(FLEHS I & II): dose-effect relationships between biomarker concentrations in urine and serum of Flemish adolescents and hormones and sexual maturation

Abstract

In 2002, the Centre for Environment and Health in Flanders (Belgium) started a human biomonitoring program (FLEHS I). For 1679 adolescents residing in nine study areas with differing pollution pressure, exposure to the pesticides p,p'-DDE and HCB, hormone levels and the degree of sexual maturation were measured. Possible confounding effects of lifestyle and personal characteristics were taken into account. In 2007, a second cycle of the Flemish human biomonitoring program (FLEHS II) started. The main purpose was generating reference values for several biomarkers, both of exposure and effect, and establishing dose-effect relationships. In this survey, not only the pesticides p,p'-DDE and HCB, but also metabolites from organophosphate pesticides and para-dichlorophenol (2,5-DCP), a metabolite of para-dichlorobenzene, were estimated. Data on internal exposure of the pesticides p,p'-DDE and HCB showed a positive

correlation with sexual maturation and the aromatase index for boys and with free T4 (both boys and girls), while a negative association with sexual development in girls was found. For HCB, a positive correlation was also found with testosterone and pubic hair development (boys) and TSH levels in the blood (boys and girls).

The organophosphate pesticide metabolites were negatively associated with sex hormone levels in the blood of the boys and with sexual maturation (both boys and girls). The pesticide metabolite 2,5-DCP was negatively correlated with free T4, while a positive association with TSH was reported (boys and girls).

These results show that even a relatively low concentration of pesticides can have significant influences on hormone levels and the degree of sexual maturation in 14-15 year-old adolescents

Keywords

Endocrine disruption, pesticides, FLEHS, hormones, human biomonitoring, sexual development.

Introduction

The Flemish Environment and Health Study (FLEHS) of 1999, a preliminary small scale biomonitoring study, provided some evidence to suggest that levels of internal exposure to pollutants were associated with observable differences in effect markers (Den Hond et al. 2002; Koppen et al. 2002; Staessen et al. 2001; Van Den Heuvel et al. 2002; Van Larebeke et al. 2006). Therefore, in 2002, the Centre for Environment and Health in Flanders (Belgium) started a human biomonitoring program (FLEHS I, 2002-2006). For 1679 adolescents exposure to the pesticide metabolite p,p'-dichlorophenyldichloroethylene (p,p'-DDE) and hexachlorobenzene (HCB), hormone levels and the de-

gree of sexual maturation were measured. In 2007, the second cycle of the Flemish human biomonitoring program (FLEHS II, 2007-2011) started. The main purpose was generating reference values for several biomarkers, both of exposure and effect, and establishing dose-effect relationships. In this survey, not only the pesticides p,p'-DDE and HCB, but also metabolites from organophosphate pesticides and para-dichlorophenol (2,5-DCP), a metabolite of para-dichlorobenzene, were measured.

The goal of this presentation is to determine the possible associated health effects between the pesticides, measured in the serum and urine of the Flemish adolescents between 2003 and 2011, and hormone levels and data on sexual maturation.

Methods and Materials

Selection and recruitment of the participants

In both the FLEHS I and II studies, 14-15 year-old adolescents were recruited in Flanders (Belgium). During FLEHS I, 1679 adolescents were recruited in 9 areas in Flanders with a different pollution pressure (two industrial sites, two harbours, two cities, a rural area, a zone around waste incinerators and a fruit cultivating

area), while in the FLEHS II study 200 participants were recruited around the whole Flanders (reference group) and 400 in two industrial hotspot regions. Sampling was performed between October 2003 and July 2004 (FLEHS I) between May 2008 and February 2011 (FLEHS II). The study design was approved by the medical-ethical committee of the University of Antwerp.

Statistical data treatment

Geometric means with 95% confidence intervals were calculated for the reference populations of respectively 1679 (FLEHS I) and 200 (FLEHS II) adolescents using SAS 9.2. To define dose-effect relationships, stepwise multiple regression analysis with correction for pre-defined confounders and selected covariates was done. Confounders for the pesticides HCB and p,p'-DDE were sex, age, BMI, smoking behaviour and amount of blood fat when expressed per amount of serum. Confounders for the organophosphate metabolites and 2,5-DCP were sex, age and the amount of creatinine when expressed per volume of urine. Confounders of data on testosterone, reaching the adult stage of testosterone, estradiol, and the aromatase index (ratio testosterone/ estradiol) were age, smoking, hour of blood sampling and

BMI. The parameters "illness during the last 14 days" and season were added as covariates to the multiple regression models. Confounders of data on LH and FSH were age, BMI and smoking. Confounders of data on SHBG were age, BMI, smoking and having not eaten before sampling of the blood, while alcohol consumption was added as a covariate. Confounders of data on sexual development were age, BMI and smoking. Confounders of data on thyroid hormones were age, BMI, sex and illness during the last 14 days. The LOQs in urine samples were 3 µg/L for DMP and DMTP; 1 µg/L for DMTP, DMDTP and DETP; 2 µg/L for DEP, DEDTP and 0.4 µg/L for 2,5-DCP. The LOQs for HCB and p,p'-DDE yielded 20 ng/L serum. For samples below the limit of quantification (LOQ), half of the LOQ was used for calculations.

Results

Dose-effect relationships: Sex hormones and degree of sexual maturation

The sex hormones (total and free testosterone, reaching the adult stage of total and free testosterone, total and free estradiol, the aromatase index, sex hormone binding globulin SHBG, luteinizing hormone LH and follicle stimulating hormone FSH) were only measured in the blood of the boys participating in the studies. The data

on sexual development were obtained for both boys and girls.

In the FLEHS II survey, HCB was positively correlated with total testosterone ($p=0.004$), reaching the adults stage of testosterone ($p=0.04$, $OR=1.29$), the aromatase index ($p=0.007$) and pubic hair development ($p=0.052$, $OR=1.77$). For girls, a negative association with reaching menarche at the age of 14-15 years old ($p=0.03$, $OR=0.39$) was reported. The pesticide metabolite p,p' -DDE was negatively correlated with breast development in girls ($p=0.03$, $OR=0.74$), while a positive correlation with the aromatase index ($p=0.02$) in boys was observed. A positive association between HCB and free ($p=0.002$) and total ($p=0.0001$) testosterone, the aromatase index ($p=0.0007$) and pubic hair development ($p<0.0001$) was also found for the boys in the FLEHS I study (Dhooge et al. 2011). In this previous study, also positive relationships between p,p' -DDE and pubic hair development ($p=0.002$) and genital development ($p=0.001$) in boys and between HCB and total estradiol ($p=0.0001$) in boys were observed, but this could not be confirmed in the FLEHS II survey.

The sum of organophosphorus pesticide metabolites (both methyl and ethyl metab-

olites) were significantly negatively correlated with free estradiol concentrations in the blood of the boys ($p=0.03$ for methyl group and $p=0.01$ for the ethyl group, both after Ln transformation). The sum of the ethyl metabolites was also negatively associated with free testosterone ($p=0.04$, after Ln transformation) and reaching the adult stage of free testosterone ($p=0.04$, $OR=0.53$, after Ln transformation). For the girls, negative associations were found between the sum of ethyl metabolites and breast development ($p=0.048$, $OR=0.78$), while for the boys a negative relation between sum of methyl metabolites and genital development was observed ($p=0.04$, $OR=0.46$).

Dose-effect relationships: thyroid hormones

Dose-effect relationships on thyroid hormones (thyroid stimulating hormone TSH, free triiodothyronine ft_3 and free thyroxine ft_4) were established for all adolescents.

In the FLEHS II survey, the pesticides p,p' -DDE and HCB were positively correlated with ft_4 ($p=0.02$ and 0.08 , respectively), while for 2,5-DCP a negative association was found ($p=0.001$). TSH was positively associated with HCB

($p=0.02$) and 2,5-DCP ($p=0.02$). No significant relationships with ft_3 were found in the latest study, but a positive association between ft_3 and HCB ($p=0.006$ for girls and $p=0.046$ for boys; unpublished results) was reported in FLEHS I.

Conclusion

The data on internal exposure of the pesticides p,p' -DDE and HCB indicated a faster sexual maturation in boys, while for girls signs of a delayed development were found. Thyroid hormones, especially ft_4 , showed positive associations with these persistent, chlorinated pesticides. Similar observations were found for the marker PCBs and several hydroxylated PCBs (unpublished results), indicating similar mechanisms of action. Dose-effect relationships for organophosphate pesticide metabolites showed the association with delayed sexual development for both boys and girls, while the pesticide metabolite 2,5-DCP seemed to have an influence on the concentrations of thyroid hormones in the blood of boys and girls (negative effect on ft_4 and a positive association with TSH). These results might imply that even a relatively low concentration of pesticides can have significant influences on hormone levels and the degree of sexual maturation in 14-15 year-old adolescents.

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ORGANOCHLORINE PESTICIDES AND HEALTH IN CHAPAEVSK, RUSSIA,

TWO DECADES OF EPIDEMIOLOGICAL STUDIES

Chapaevsk (population 72,000) is a small city located in Central Russia (950 km south-east of Moscow), half of its area was occupied by chemical industries. The Chemical Plant produced chlorine-containing industrial and agricultural chemicals, such as the organochlorine pesticides (OP), including hexachlorobenzene (HCB), and beta-hexachlorocyclohexane (HCH) from 1967 to 1987, which generated polychlorinated dibenzodioxins/dibenzofurans (PCDD/PCDFs) as industrial contaminants (Revich et al. 2001). By 2003, the production of all chemicals at that plant ceased. Environmental contamination by OP may have resulted from improper disposal, storage of hazardous waste from factories, or environmental release of organochlorine by-products of the manufacturing process (Shelepchikov et al. 2008).

Since 1994, ecological studies conducted in Chapaevsk to estimate OPs/dioxin levels in blood, milk, and to assess cancer risks and reproductive health status. High levels of these compounds have been detected in serum and milk samples from Chapaevsk residents, as well as in environmental samples and food (Akhmedkhanov et al. 2002; Revich et al. 2001). The male cancer mortality observed rate in Chapaevsk was higher than expected, especially for lung cancer and urinary organs. Further studies have demonstrated the effects on semen quality among worker of plant (Goncharov et al. 1999), an increased rate of breast cancer in women working at the plant and local residents who eat contaminated pork or fish (Revich et al. 2002).

Since 1998, international team from Rus-

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sia and Harvard School of Public Health conducted a pilot cross-sectional study of growth and pubertal outcomes among 2516 Chapaevsk boys at the age of 10-16 years (Lee et al. 2003). We presented elevated frequency of cryptorchidism, varicocele and delayed puberty among these adolescents (Sergeyev et al. 2000). In 2003, this was followed by establishing a longitudinal cohort of 516 families, called the Russian Children's Study, with primary objectives of examining the predictors of prepubertal serum organochlorine compounds among the Chapaevsk boys and evaluating their associations with the measures of physical growth, sexual maturation, reproductive health and biological markers.

We have discovered higher median serum levels of HCB and β -HCH among 355

boys of 8-9 years in comparison with other populations (158 and 167 ng/g lipid, respectively). Lower body mass index, longer breastfeeding duration, local dairy consumption, close residence to chemical plant and long residence in Chapaevsk were associated with higher prepubertal concentrations of OPs (Lam et al. 2013). In adjusted models, serum OP concentrations measured at 8–9 years of age were associated with reduced growth, particularly reduced BMI, during the peripubertal period of 4 years of follow-up (Burns et al. 2012). Higher serum HCB was associated with higher serum insulin, and the odds of insulin resistance over 4 years of follow-up (Burns et al. 2011). Higher prepubertal serum OP concentrations were associated with a later age of attainment of sexual maturity measures over 7 years of follow-up (Lam et al. 2013).

Since 1997, simultaneously with studies, there were environmental remediation and social rehabilitation programs, financed by the Russian, regional and local governments in Chapaevsk. Soil in Chapaevsk was remediated and mean dioxins TEQ in breast milk of Chapaevsk citizens declined 3.8 times over the ten year time period, from 41.1 pg/g lipids in 1998 to 10.9 pg/g lipids in 2007 (Sergeyev et al. 2008). Based on our recent study, (Sergeyev et

al. 2013) we could observe a secular trend towards increased linear growth, BMI and earlier attainment of sexual maturity during the 10 to 14 year period (from 1999 to 2012/13) among the adolescents of Chapaevsk.

HUMAN CONTAMINATION BY PERSISTENT TOXIC SUBSTANCES

PROPOSALS TO IMPROVE EXPOSURE ASSESMENT

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Worldwide, most health information systems on chemical body burden and, specifically, on the population distribution of human contamination by persistent toxic substances (PTS) are weak and incomplete, if they exist at all. Unfortunately, in many countries, public health, preventive medicine, and medicine at large, are currently not properly assessing such exposures and their health effects (Gasull et al., 2013; Kolossa-Gehring, 2012; Porta et al., 2008, 2012a; Porta, 2012; Viso et al., 2009). It is important that this situation changes as soon as possible. With some exceptions (see references in Kolossa-Gehring, 2012; Patel et al., 2012; Porta et al., 2008), there are few population-based, systematic and comprehensive analyses of the exposure to and the effects of common environmental contaminants on clinical outcomes and clinically-relevant physiological endpoints (CDCP, 2009; Lee et al., 2009; Porta et al., 2008, 2010; Weinhold, 2003). Many such pollutants are known to alter a range of physiological functions significantly, and

known or reasonably suspected to contribute to cause severe clinical effects, as well as a substantial burden of disease (Alonso-Magdalena et al., 2011; Barouki et al., 2012; Casals-Casas and Desvergne, 2011; Engel and Wolff, 2013; Henkler and Luch, 2011; Hernández et al., 2009; Hou et al., 2012; Manikkam et al., 2012; NRC, 2006, 2008; NTP, 2011; Peters et al., 2012; Porta, 2004, 2006; Prüss-Ustün et al., 2011; Soto and Sonnenschein, 2011; Swedenborg et al., 2009; Vandenberg et al., 2012).

Some highly prevalent chemical agents and chemical mixtures have immune-disrupting, oxidative, proinflammatory, neurotoxic, neuroendocrine, nephrotoxic, metabolic, carcinogenic, non-genotoxic or epigenetic properties and effects (Alonso-Magdalena et al., 2011; Barouki et al., 2012; Casals-Casas and Desvergne, 2011; CDCP, 2009; Henkler and Luch, 2011; Hernández et al., 2009; Hou et al., 2012; Lee et al., 2009; Manikkam et al., 2012; Morrens et al., 2012; NRC, 2006, 2008; NTP, 2011; Peters et al., 2012; Porta,

2004, 2006; Soto and Sonnenschein, 2011; Swedenborg et al., 2009). Scientific evidence on such effects is often neglected, disregarded or downplayed in the biomedical literature and by institutions and organizations. Such toxic exposures may also partly explain important disease-disease associations; e.g., between some cancers and obesity, diabetes, autoimmune or inflammatory disorders (Gasull et al., 2012; Porta et al., 2009, 2012). Furthermore, at present, the functional properties of many environmental agents are better known than those of many genetic loci. Throughout the life course, key causal processes in the etiopathogenesis of some highly prevalent human diseases involve chronic contamination by persistent toxic pollutants and the ensuing accumulation of genetic and epigenetic alterations. In this respect, we should reflect on these words from the editor of *The Lancet*: “And why has the gene revolution failed so spectacularly to deliver anything tangible for patients? Because we have underestimated, even wilfully disregarded, the complexity

of disease. Our indifference to physiology—to an understanding of systems in disease—has been a catastrophic loss to medicine” (Horton, 2011).

In my view, the available evidence indicates that we are not assessing comprehensively to what mixtures is the general population significantly exposed in critical periods of life, how many persistent toxic pollutants we accumulate during the life course, or even the number of chemicals whose continued presence in the human body it is most relevant to analyze (Porta et al., 2008, 2012a, 2012b, 2013). However, some studies suggest that citizens of the postindustrial economies often accumulate mixtures of 50, 70, 100 or even more toxic agents (ContamiNation, 2003; Watson, 2005; Weinhold, 2003; Woodruff et al., 2011).

In Catalonia, for instance,

- 73% of the population accumulates 10 or more persistent organic pollutants (POPs) (of only 19 analyzed);

- 34% of citizens have concentrations in the top quartile of ≥ 3 of the 8 most frequent POPs;

- over 30% of the population has concentrations in the top decile of 1 to 5 of the 8 most prevalent POPs;

- half of the population has levels of 1 to 5 POPs >500 ng/g;

- among women 60–74 years old (a subgroup with an obviously high incidence and prevalence of morbidity),

- a) 83% have concentrations of ≥ 3 POPs in the top quartile, and

- b) 48% have concentrations of ≥ 6 POPs in the top quartile;

- less than 4% of the Catalan population has concentrations of all the 8 most common POPs in the lowest quartile (Porta et al., 2010, 2012b, 2013).

Hence, it is not accurate to state that most of the population has low concentrations of POPs: contamination from selected toxic chemicals is common at high and low concentrations (Porta et al., 2012b).

In summary, I invite you to integrate in your own framing these issues:

- a) we know quite a lot about the generalized human contamination by environmental chemical agents (a statement that is fully compatible with the assessment that most countries lack the necessary monitoring systems) (Porta et al., 2008);

- b) we also know quite a lot about the tox-

ic effects of environmental pollutants (a statement that is fully compatible with the proposal that we need both more research, and more energetic policies to decrease human contamination by such pollutants); and

- c) we know too little about the causes and the etiopathogenesis of the most prevalent diseases, and we will continue to miss relevant causes and mechanisms if we neglect toxic chemicals.

Or we may put it this way: when we do not integrate biomarkers of internal dose of environmental pollutants in our research on the etiopathogenesis of human diseases of complex etiology,

1. we are trying to study ‘something’ that hardly exists (fully uncontaminated human beings);

2. our causal inferences are less likely to be relevant for human health; and

3. we are likely to miss causes and mechanisms of the processes that we aim to study (e.g., causes of changes in gene expression, of accumulation of genetic defects, of alterations in metabolic functions). Knowledge on the joint effects of ‘chemical cocktails’ during the life course ought to be used more often when building

causal scenarios that aim at being relevant for human health.

It is hard to explain why human contamination by environmental chemical agents is not integrated deeply into medicine and, more generally, into basic, clinical and epidemiological research (Alonso-Magdalena et al., 2011; Barouki et al., 2012; Casals-Casas and Desvergne, 2011; ContamiNation, 2003; Gasull et al., 2012; Henkler and Luch, 2011; Hernández et al., 2009; Horton, 2011; Hou et al., 2012; Howard and Lee, 2012; Hoyo et al., 2009; Kauffmann and Nadif, 2010; Lee et al., 2009; Lee and Jacobs, 2010; Manikkam et al., 2012; NRC, 2006, 2008; NTP, 2011; Peters et al., 2012; Porta, 2004, 2006, 2008, 2009; Porta and Álvarez-Dardet, 1998; Porta et al., 2009; Soto and Sonnenschein, 2011; Stein, 2012; Swedenborg et al., 2009; Tickner, 2011; Vandenberg et al., 2012; Watson, 2005; Woodruff et al., 2010, 2011). There is strong evidence showing that scientific neglect of toxic chemicals is partly due to investigators', institutional, political and social biases, including academic, cultural and economic influences (Greenland, 2012; Michaels, 2008; Porta, 2008).

May I thus also suggest that we should more often seriously consider integrating biomarkers of internal dose of environ-

mental chemical pollutants in our efforts to prevent human diseases. When we neglect less the generalized human contamination by environmental chemical agents and their toxic effects, we will expand mechanistic biologic knowledge, and we shall as well increase the effectiveness of interventions and policies that enable the primary prevention of diseases that cause a huge economic burden and human suffering.

Conflict of interest statement

The author declares no competing interests.

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NEUROTOXICITY OF PERSISTENT ORGANIC POLLUTANTS WITH SPECIAL REFERENCE TO PCBS AND AUDITIVE FUNCTIONS

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POPs include many different organic chemicals with common properties such as long-persistence, widespread diffusion in the environment, and accumulation in fatty tissues of living organisms. A growing body of scientific evidence associates human exposure to POPs with various health outcomes, including neurodevelopmental impairment. These effects may be elicited by mechanisms such as endocrine system disruption, oxidative stress, or epigenetic mechanisms, though the exact mechanisms are not clear. Many laboratory studies have been carried out using unrealistically high doses which makes extrapolation with regard to environmental human exposures very difficult. However, as a whole, a recently published literature search shows that the epidemi-

ologic studies did not strongly implicate any particular organochlorine pesticide as being causally related to adverse neurodevelopmental outcomes in infants and children. Future work in this area may be improved by the addition of more sensitive outcome measures for the evaluation of neurodevelopmental damages induced by chemicals. For instance, we have successfully introduced into epidemiological research of neurotoxic effects of PCBs the measurements of otoacoustic emissions (OAEs). These methods have been applied in experimental studies in animals, however they have not been used extensively in epidemiologic investigations. Data from studies in the Slovak Republic among children and adolescents, show adverse associations between PCB exposures and

OAEs, and therefore PCBs may have the potential to damage the outer hair cells of the cochlea. Moreover we have shown that child, rather than maternal or infant PCB concentrations are associated with poorer performance on otoacoustic tests of cochlear status at age 45 months, suggesting a possible short-term effect. We have undertaken preliminary steps to apply the OAE methodology to other POP exposures, such as HCB and HCH.

HEALTH PROBLEMS AT OBSOLETE PESTICIDES SITES (EXPOSURES AND TOXICITY OF PESTICIDES)

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The symposium on exposure and effects of HCH and POP pesticides should assist to answer the following questions:

1. Can low levels of persistent pesticides be detected in biological fluids (serum, urine, milk) or tissues (fat, organs) of exposed humans?
 2. Does exposure to dump and waste sites or landfills containing persistent pesticides lead to changes in internal levels (= biomarkers of exposure) of these pollutants in people living in neighbourhood areas?
 3. Will such elevated levels of pollutants be relevant enough to induce biological effects? And: What kind of effects could be expected in the exposed human and animal populations?
-

Exposure and Effects of Pesticides
Reproduction
The FLEMISH Environment and Health studies in Flanders, Belgium illustrate

the clear dependence of human pollutant levels from pollutant pressure in designated areas: Adolescents residing in study areas with slightly differing densities of contamination also differed with regard to serum levels of pollutants. Biomonitoring samples of study participants living in areas of waste incinerators had significantly elevated blood and urine levels. Also sex hormone concentrations were increased. However, differences in hormonal levels and sexual maturation could only in part be explained by differences in internal levels of contaminants and may also be due to differing individual pollutant patterns and yet unknown factors (Croes et al., 2009).

Another study reported on a cohort of 8–9 year old boys in Chapaeusk, a small city in Central Russia, where half of the city was occupied by chemical industries producing chlorine containing agricultural chemicals including HCB and HCHs. OCP (organochlor pesticide) concentrations were found to be associated with total time living in Chapaeusk, distance from OCP

source, but also with local dairy consumption, longer duration of breast feeding and lower BMI in these children (Burns et al., 2009).

In the city of Ufa, a hot spot of dioxin pollution, higher dioxin concentrations were found in ejaculate of men diagnosed as infertile. High dioxin levels were also associated with pathospermia (Gromenko et al., 2008).

Cancer

Excess cancer risk is increasingly found to be associated with abundant use of pesticides in agricultural, commercial and home and garden applications. Positive associations are also found between childhood leukemia and pesticide exposures. Other studies suggest that occupational agents like chlorinated solvents or organochlor compounds (PCBs) may play a role in the causation of exocrine pancreatic cancer, while DDT's association with breast cancer has been described repeatedly (Alavanja et al., 2003; Meinert et al.,

2000). Exposures remain high: New studies report that more than half of the study population in Spain had concentrations in the top quartile of ≥ 1 POPs (Bosch de Ba-sea et al., 2011).

Neurotoxicity

In more recent systematic reviews on neurodevelopmental outcomes of children exposed to pesticides (organophosphates, organochlorines), PCBs, mercury, cadmium and/or lead during early life, the majority of studies indicate a negative impact.

There is increasing evidence that chemicals present in the environment can interrupt neurodevelopmental processes during critical periods of development, with adverse effects on structure and function, leading to functional disturbances in children, adolescents and adults. Exposed neonates can exhibit, i.a., hearing loss, higher proportion of abnormal reflexes, while young children show more attention deficits and other behavioral problems.

Important to know: Neurodevelopmental disorders like autism, ADHD (attention deficit and hyperactivity disease), mental retardation and cerebral palsy are common, costly and are all lasting for lifetime (Trnovec et al., 2010; Jurevicz et al., 2013).

Liver diseases

Brazils Santos and São Vicente Estuary suffers from contamination by toxic industrial waste. Prevalence of liver disease, hepatitis, cirrhosis and liver, biliary tract or pancreas cancer was evaluated in a study at St. Paulo University, Brazil. Occupational exposure to chemicals, alcohol consumption, consumption of locally produced milk and fruit, and water from natural sources, appeared as risk factors for liver diseases (Carvalho et al., 2013).

In conclusion, there is evidence from more recent international studies presented at the symposium in Kiev that elevated exposures to persistent organochlorines and other pesticides can occur in proximity to dump and waste sites or landfills and affect biomarkers of exposure (concentrations of chemicals in the environment) and have detrimental effects on exposed human and animal populations. Especially at risk are early life stages with respect to reproductive and neurodevelopmental effects (fetal origin of adult diseases). Additional areas of concern are cancer in young and adult life, liver diseases and derailed energy metabolism, which is increasingly attracting attention.

All of the aforementioned aspects deserve more attention and need more scientific input, i.a., advances in analytical proce-

dures (Pieterse et al., 2013). Finn Bro-Rasmussen pointed out that environmental pollution is still ongoing more or less unimpededly regardless of new chemical legislations (REACH), and that it remains difficult to cope with the situation (Bro-Rasmussen et al., 2013). It would be important to demonstrate reduced levels of internal exposures associated with occurrence of changes in biological parameters following clean-up of chemical waste sites in order to strengthen correlations between exposures and biological consequences.

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INVENTORY, MONITORING AND RISK ASSESMENT



**PESTICIDES SPREAD FROM NUBARASHEN
OBSOLETE PESTICIDES BURIAL SITE (ARMENIA)
(SUBMITTED PAPER)**

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Abstract

In 1980s the special place was allotted for pesticides burial near Nubarashen village in the vicinity of Yerevan – capital city of Armenia. At the territory of the organized burial site about 500 tons of obsolete pesticides were buried; the volume of organochlorine pesticides made 250 tons.

In 2012, in order to assess the pollution and the real threat, sampling and laboratory analyses of soil taken from neighboring sites were done. Sampling was done from the plots beginning the entrance to the burial site, directly above the burial site and was continued up to inhabited settlements of Mushavan and Jrashen. Eighteen average samples were taken, among which 5 were from plots of Jrashen and Mushavan. The samples were analyzed for organochlorine POPs pesticides.

Visualization of analytic results for DDT and its metabolites, as well as HCH iso-

mers was of special attention. Soils from the outward nearest plots on the average contained 1.4 mg/kg DDT, while soils from the same plots, if sampled from the depth of 20 cm, contained on the average 2.3 mg/kg DDT. Soil taken directly from the burial site contained about 59 mg/kg DDT, while soil near the drainage tube contained 13.5 mg/kg. Below the burial, soil taken from the depth of 1 m contained on the average 1.6 mg/kg p,p'-DDE and 6-8 mg/kg p,p'-DDT. In the same direction at a distance of 20 to 100 m the amount of DDT in samples of soil made appropriately 1.1 and 0.2 mg/kg. At the plots of summer houses below the burial (>500 m) residues of p,p'-DDE made 0.008 mg/kg, whereas p,p'-DDT = 0.04 mg/kg. In samples of soils from Mushavan and Jrashen DDT averaged from 0.005 to 0.01 mg/kg.

Nubarashen burial site of obsolete pesticides in the vicinity of Yerevan is an object of visual pollution.

Keywords

Obsolete pesticides; burial site; persistent organic pollutants; DDT; HCH.

Article

The burial site of obsolete pesticides near to Yerevan City is an object of visual pollution. The problem of obsolete and banned pesticides became mostly urgent since late 1970s, when there arose the necessity of final disposal (burying) of obsolete and banned pesticides (mainly organochlorine ones) accumulated at the territory of Armenia.

In early 1980s, the special place was allotted for pesticides burial near Nubarashen

village. At the territory of the organized burial place about 500 tons of obsolete pesticides were buried (finally disposed), of which the volume of organochlorine pesticides made 250 tons [Aleksandryan A. et al., 2003].

The complexity of the problem dealing with the obsolete pesticides burial is worsened by the fact that the site allotted for this burial is located in the zone of active landslide processes, which can cause damage, crippling and a possible breakthrough of the “innage” and subsequent penetration of residues of buried obsolete pesticides, including organochlorine ones, into the environment resulting in environmental pollution [Aleksandryan A., 2005].

The problem of Nubarashen pesticides burial site, in particular, its environmentally sound liquidation (elimination) is stated in the National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants [Aleksandryan A. et al., 2004].

After the infringement of the burial site integrity, due to unclear reasons, there actually occurred a secondary pollution of the environment by mentioned pesticides. In 2010 the Ministry of Nature Protection performed activity on conservation of the

burial site, covering the Nubarashen pesticides burial site, repairing the drainage system and fencing.

In 2012, in order to assess the degree of impurity and pollution scales and for assessment of the real threat, sampling and laboratory analyses of soil taken from neighboring sites were done to determine soil pollution by the buried pesticides. Average samples were taken using “envelope” method and then provided to the Laboratory.

Sampling was done from the plots beginning at the entrance to the burial site, directly above the burial site and was continued up to inhabited settlements of Mushavan and Jrashen. Upon sampling, we took into consideration the localization of the burial site on the slope of the hill, as well as the summer houses located at the lower level. Taking into consideration the fact that pollution might have originated only in the direction of downwards placed plots, sampling was done precisely in that direction. The samples were analyzed for organochlorine POPs pesticides.

Visualization of analytic results for DDT and its metabolites, as well as HCH isomers was of special attention. Comparing the results of analyses with the topographic location of the plots, we found that

soils from the outward nearest plots on the average contained 1.4 mg/kg DDT, while soils from the same plots, if taken from the depth of 20 cm, contained on the average 2.3 mg/kg DDT. Soil taken directly from the burial site contained about 59 mg/kg DDT, while soil near the drainage tube outgoing from the burial contained 13.5 mg/kg. Below the burial, at the fence from the outward part, soil taken from the depth of 1 m contained on the average 1.6 mg/kg p,p'-DDE and 6-8 mg p,p'-DDT. In the same direction at a distance of 20 to 100 m the amount of DDT in samples of soil made appropriately 1.1 and 0.2 mg/kg.

At the plots of summer houses below the burial (>500 m) the residual amount of p,p'-DDE made 0.008 mg/kg, whereas p,p'-DDT = 0.04 mg/kg. In samples of soils taken at the settlements Mushavan and Jrashen the amount of DDT, on the average, made from 0.005 to 0.01 mg/kg.

Table: Results of analyses for POPs pesticides in samples of soil taken from the Obsolete Pesticides Burial Site, mcg/kg, 2012

NN	Sampling points	Organochlorine pesticides										
		α -HCH	HCB	β -HCH	γ -HCH	Heptachlor r	o,p'-DDE	p,p'-DDE	o,p'-DDD	p,p'-DDD	o,p'-DDT	p,p'-DDT
1	Sampling point 1: directly at the entrance of the burial site	7.0	7.1	53.8	12.2	8.0	34.2	128.1	27.1	110.2	453.3	1425.5
2	Sampling point 2: the same point from a depth of 20cm	28.5	11.3	95.7	15.2	7.2	102.7	171.6	44.2	201.3	687.8	2390.2
3	Sampling point 3: near drainage tube (lower boundary of the burial)	33.7	108.2	213.0	23.5	6.3	780.0	1149.6	323.5	1230.8	3842.4	13504.5
4	Sampling point 4: directly from the surface of the burial	281.2	230.9	461.7	233.6	44.6	3888.0	3675.2	1136.0	3765.3	12964.6	59816.4

5	Sampling point 5: the lower boundary of the burial	63.7	59.1	648.6	33.7	19.8	769.3	1554.1	237.5	758.2	2320.1	8320.5
6	Sampling point 6: the lower boundary of the burial (1 m from burial surface down the hill)	22.2	11.4	103.2	20.0	10.9	728.2	1613.3	163.8	439.0	1596.2	6300.7
7	Sampling point 7: at a distance of 20 m from the lower fence of the burial site	4.6	3.6	34.3	12.1	11.3	209.1	1250.8	56.1	65.8	485.7	1144.9
8	Sampling point 8: directly downwards from the burial site, leftwards from Aviators' summer houses (to the left)	4.2	2.5	25.3	7.7	12.2	149.4	949.7	39.3	41.7	329.4	725.2

9	Sampling point 9: at a distance of 100 m downwards from the fence of burial site	5.5	3.1	14.2	10.5	13.8	50.5	32.0	8.3	9.1	91.8	210.3
10	Sampling point 10: forefront of summer-house plot downwards from the burial site	4.7	3.2	2.0	4.6	13.1	6.5	8.3	2.4	3.4	11.5	41.9
11	Sampling point 11: the remote part of the summer-house plot (downwards), at the country road	4.4	3.1	19.7	4.6	13.9	9.1	10.1	1.9	3.0	10.7	31.5
12	Sampling point 12: downwards from the burial site at the high-way	4.2	2.5	23.6	5.5	14.4	3.6	5.5	2.7	2.6	7.1	24.5
13	Sampling point 13: 100 m below summer houses	7.3	6.1	21.7	10.6	14.6	12.1	29.2	4.9	8.2	31.6	86.7

The analysis of data obtained allows to draw conclusion that the actual migration does not deal with the temporal migration of pesticides, while pollution is caused by disintegration of the burial site and the follow-up recovery works. As a result, there

occurred a certain spread of pesticides into the soil of nearby plots; to this latter indicate the analyses of soils from the plots in the direct vicinity to the burial site.

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RESIDUES OF ORGANOCHLORINE PESTICIDES IN SURFACE WATERS OF ARMENIA (SUBMITTED PAPER)

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Abstract

Within the frames of monitoring studies performed in 2012 for residual amounts of Persistent Organic Pollutants (POPs) in different environmental media samples of water from the Lake Sevan and rivers of Armenia were analyzed.

Residues of POPs pesticides were revealed in studied samples of surface water with the help of “Gas-Chromatograph/Mass-Spectrometer GCMS-QP2010 SE EI 230V CELV incl. GC-2010 Plus” (Shimadzu Corporation, Japan).

According to research findings, in all tested samples of surface water the residual amounts of pesticides were revealed at microgram (μg) levels:

- Hexachlorocyclohexane isomers varied from 0.006 to 1.1 $\mu\text{g/L}$;
- DDT and its metabolites made 0.004-0.5 $\mu\text{g/L}$;
- Heptachlor amounted 0.1- 0.86 $\mu\text{g/L}$;
- Hexachlorobenzene made 0.09-0.3 $\mu\text{g/L}$;
- Aldrin: 0.01-0.3 $\mu\text{g/L}$;
- Dieldrin: 0.01-0.2 $\mu\text{g/L}$;
- Endrin: 0.02-0.2 $\mu\text{g/L}$;
- Mirex: 0.01-0.1 $\mu\text{g/L}$.

The summary quantity of HCH isomers in analyzed samples of water varied in the range of 0.00013-0.0014 mg/L, while

DDT and its metabolites made 0.00002-0.0015 mg/L.

DDT was determined only in Masrik and Gavaraget rivers; in other water basins only products of DDT degradation were found: DDE and DDD.

The comparison of research results obtained in 2012 with earlier data of 2002-2003 demonstrated that the tendency was observed to a significant decrease of organochlorine substances residual amounts in surface water of Armenia.

Keywords

Monitoring studies; persistent organic pollutants (POPs); surface water; residual amounts.

Article

Within the frames of monitoring studies performed in the Republic of Armenia in 2012 for residual amounts of Persistent Organic Pollutants (POPs) in different environmental media 12 samples of water from the Lake Sevan and rivers of Armenia were analyzed.

For measurements in water of open reservoirs of the Republic of Armenia DDT, HCH, Lindane (γ -HCH), Heptachlor and Hexachlorobenzene were chosen from the list of pesticides regulated by the Stockholm convention. The first three pesticides had production value and for many years were applied as means of pest control and against diseases of plants almost in all agricultural regions of the country. Heptachlor was used, both as pesticide and as the substance with potential to be formed in various technological processes [Aleksandryan A., 2010].

Twelve samples of surface water were taken and analyzed in order to investigate the content of OCPs.

The study involved rivers Masrik, Martuni, Gavaraget, Hrazdan, as well as Sevan Lake and water reservoirs (storage ponds) "Yerevanyan" and "Akhpara".

Sampling was done according to the uni-

fied method for samples taking followed by determination of pesticides residual amounts.

The average water samples analyzed using Gas-Chromatography method for 15 pesticides, including those of interest: DDT and metabolites, HCH isomers, Heptachlor, Hexachlorobenzene, Aldrin, Dieldrin, Endrin, and Mirex. Residues of POPs pesticides were revealed in studied samples of surface water with the help of "Gas-Chromatograph/ Mass-Spectrometer GCMS-QP2010 SE EI 230V CELV incl. GC-2010 Plus" (Shimadzu Corporation, Japan).

The amounts of pesticides in studied samples were as follows:

- Hexachlorocyclohexane isomers varied from 0.006 to 1.1 mcg/L;
- DDT and its metabolites made 0.004-0.5 mcg/L;
- Heptachlor amounted 0.1- 0.86 mcg/L;
- Hexachlorobenzene made 0.09-0.3 mcg/L;
- Aldrin: 0.01-0.3 mcg/L;
- Dieldrin: 0.01-0.2 mcg/L;

- Endrin: 0.02-0.2 mcg/L;

- Mirex: 0.01-0.1 mcg/L.

According to study results in all tested samples the residual amounts of pesticides were revealed at mcg levels, whereas in 2002-2003 the content of pesticides (DDT and its metabolites, heptachlor, HCH and its isomer, as well as hexachlorobenzene) in samples of water from open reservoirs of Armenia exceeded standards of these substances in water of reservoirs [Khachatryan A. et al., 2004; Aleksandryan A., 2006].

There are different Maximum allowable concentrations (MACs) for water of open water reservoirs for household use.

In water of open water basins intended for fishery no residual amounts of HCH and its isomers, DDT and its metabolites are allowed.

MACs of HCH and its isomers, DDT and its metabolites in samples of water taken from open water basins intended for agricultural use make 0.02 mg/L and 0.1 mg/L, appropriately.

MACs of HCH and DDT in drinking water make 0.002 mg/L.

DDT was determined only in Masrik and Gavaraget rivers; in other water basins only products of DDT degradation were found: DDE and DDD.

In analyzed samples of water the summary quantity of HCH isomers varied in the range of 0.00013-0.0014 mg/L, while DDT and its metabolites made 0.00002-0.0015 mg/L.

Table 1: POPs Pesticides: Residues in samples of water from Sevan Lake and rivers of Armenia, 2012 (meg/L)

NN		Organochlorine pesticides														
		α -HCH	HCB	β -HCH	γ -HCH	Heptachlor	Aldrin	o,p'-DDE	p,p'-DDE	Dieldrin	o,p'-DDD	Endrin	p,p'-DDD	o,p'-DDT	p,p'-DDT	Mirex
1	Water, Masrik River	0.254	0.072	0.404	0.130	0.860	0.200	0.202	0.052	0.012	0.054	0.052	N/R	0.028	0.086	0.318
2	Water, Martuni River	0.026	0.034	0.092	0.006	0.168	0.010	0.046	N/R	N/R	0.018	N/R	N/R	N/R	N/R	0.184
3	Water, Sevan Lake near Airivank Village	0.020	0.036	0.058	0.018	0.380	0.032	0.084	N/R	N/R	0.032	N/R	N/R	N/R	N/R	0.082
4	Water, Gavaraget River	0.884	0.188	1.216	0.412	3.310	0.356	0.538	0.180	0.034	0.244	0.346	0.050	0.244	0.392	0.074
5	Water, Sevan Lake. North-East of Small Sevan	0.008	0.010	N/R	N/R	0.082	N/R	N/R	N/R	N/R	0.008	N/R	N/R	N/R	N/R	0.064
6	Water, Sevan lake. Lchashen Bay	0.134	0.076	0.302	0.086	0.214	0.014	N/R	N/R	N/R	0.022	N/R	N/R	N/R	N/R	0.096
7	Water, Hrazdan River head	0.026	0.056	0.064	0.006	0.158	0.010	N/R	N/R	N/R	0.012	N/R	N/R	N/R	N/R	0.118
8	Water, Akhpara	0.018	0.048	0.088	0.064	0.216	0.012	0.004	0.012	N/R	0.018	N/R	N/R	N/R	N/R	0.018

NN		Organochlorine pesticides														
		α -HCH	HCB	β -HCH	γ -HCH	Heptachlor	Aldrin	o,p'-DDE	p,p'-DDE	Dieldrin	o,p'-DDD	Endrin	p,p'-DDD	o,p'-DDT	p,p'-DDT	Mirex
	Reservoir (storage pond)															
9	Water, Hrazdan River near Arzni Village	0.024	0.042	0.050		0.200	0.014	N/R	N/R	N/R	0.014	N/R	N/R	N/R	N/R	0.066
10	Water, Yerevan Reservoir (storage pond)	0.018	0.036	0.070	0.042	0.204	0.034	N/R	N/R	N/R	0.016	N/R	N/R	N/R	N/R	0.024
11	Water, Hrazdan River "Aeration" treatment station	0.040	0.024	0.068	0.012	0.632	0.026	0.082	N/R	N/R	0.030	N/R	N/R	N/R	N/R	0.038
12	Water, Hrazdan River. Masis town	0.028	0.024	0.028	N/R	0.112	N/R	N/R	N/R	N/R	0.008	N/R	N/R	N/R	N/R	0.128

The comparison of research results obtained in 2012 with earlier data of 2002-2003 demonstrated that the tendency was observed to a significant decrease of organochlorine substances residual amounts in surface water of Armenia.

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THE USE OF EFFECT-BASED ANALYSIS FOR ENVIRONMENTAL HEALTH RISK CHARACTERISATION OF POPS PESTICIDES DUMPSITES

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Abstract

One of the problems concerning dumpsites with (obsolete) POPs pesticides and other hazardous chemicals is to provide a comprehensive analysis of the environmental health risks. Typically, risks are classified by chemical screening of the source site and direct surroundings, using a predefined set of compounds, which can be unsuitable for complex mixtures and samples with unknown compounds ('black boxes'). In this paper, we present the application of effect-based testing as an alternative and complementary approach to conventional chemical analysis, using Kanibadam POPs burial site (Tajikistan) as a case-study. CALUX bio-based reporter assays are used to profile soil samples containing a complex mixture of known and unknown compounds. The results are compared with the risk assessment based on conventional chemical screening for organochlorine compounds.

It is shown that conclusions from both chemical and effect-based analysis are quite similar. Contamination levels within the burial site are, in our case, over 100 times the risk-based soil quality standards. However, the results from the effect-based analysis shows for a specific spot that additional toxicological activity is present to what can be explained by the compounds that were identified and quantified by the chemical analysis.

It is concluded that effect-based bioassays are suitable as an alternative and complementary approach to conventional chemical analysis. Effect-based analysis is especially preferred as a screening methodology for hazards, and in cases where complex mixtures are expected. To make risk assessments more comprehensive, as well as more toxicologically relevant, it is highly recommended to perform an effect-based analysis.

A remaining challenge is how to assess off-site migration of POPs and to embed this into risk assessment. Therefore, for further investigation, it is suggested to profile potential sinks that act as exposure matrices, such as meat, dairy products and fish. The effect-based analysis of such samples could provide a more realistic risk assessment for human health, taking into account ongoing accumulation and degradation in the surroundings of a POPs

Keywords

Dumpsites, POPs and hazardous chemicals, risk assessment, CALUX, bioassay, Tajikistan.

Introduction

Despite international attention to POPs, many old stockpiles and dumpsites of (obsolete) POPs pesticides and other hazardous chemicals still exist around the world. One of the problems for characterisation of the environmental quality of the soil and groundwater at these sites is that assessment is typically performed by means of the chemical analysis of a predefined set of compounds. Although this will provide an indication of the presence of the compounds and associated environmental risks, the major drawbacks are as follows: i) sites can be a 'black box' with unknown compounds dumped which are not analysed; ii) degradation results in many degradation products, which are not always analysed, or otherwise difficult to interpret; iii) interaction of various compounds are not taken into account; and (iv) analysis of a complete set of compounds, even if they are known, is often not technically and/or financially possible.

In this paper, we present the application of effect-based testing as an alternative and complementary approach to chemical analysis. CALUX (Chemically Activated LUCiferase eXpression) bio-based reporter assays are used to profile complex mixtures of soil samples from a dumpsite of

obsolete and POPs pesticides (see box). Site risks characterised with CALUX are compared to risks characterised using conventional chemical screening of soil samples for organochlorine pesticides. In this paper, the suitability of effect-based bioassays for risk characterisation of POPs polluted hazardous waste dumpsites is evaluated and recommendations are made towards its application.

Case: Kanibadam dumpsite

Kanibadam is a POPs and obsolete pesticide dumpsite, located close to the densely populated and fertile Fergana valley in Northern Tajikistan. It is estimated that about 4000 tonnes of phased out and banned pesticides were buried and burnt at Kanibadam between 1973 and 1990. The pesticides included DDT, lindane, other organochlorinated pesticides, organophosphates, arsenates and other toxic compounds. At the time of research, the site, located just 3 km upstream of the city of Kanibadam, was neither fenced nor protected.

Methodology

A topsoil sampling campaign was carried out to provide a screening on the con-

tamination level present within the burial site and its direct surroundings. From the direct surroundings, dust deposition samples, runoff samples in drains, baseline samples and samples from suspected sources outside the burial site were taken. In total, 21 composite samples have been obtained each consisting of 10 individual samples using only the upper 20 cm of soil. The samples were sieved (0.2x0.2 cm) and homogenized in the field. The samples have been analysed for the most commonly present organochlorine pesticides and their degradation products (HCH-isomers, DDT, and the "drins"). The results were normalised for organic matter content and clay fraction and screened against soil target values from the Netherlands as a Tier 1 risk assessment.

Five of these soil samples were selected for CALUX analysis, two of which from inside the burial site ('Source' and 'Gully east') and three from the surroundings ('Drain 4' 100m down from the polygon, 'Drain 5' 2 km down from the polygon, and 'Baseline wind' 200m upwind from the site).

The CALUX panel comprises mammalian cell line-based reporter assays for the

detection of over 25 distinct effects at the cellular level (e.g. endocrine disruption, dioxin receptor-mediated signalling, genotoxicity and acute toxicity). It measures the biological activity of a sample without the requirement of prior knowledge of the exact chemical composition of the sample. The CALUX assays are performed using an automated platform in 384-well plates, where biological activity is measured using a luminometer as described (Piersma et al., 2013). For this case, 8 assays were selected (Table 1).

The activities measured on the CALUX assays are expressed as biological equivalences (BEQ) relative to a reference compound. For pure compounds, the biological potencies relative to the reference compounds can be established (REP values). Comparison between chemical analytical data and bioassay data for the soil samples was done by comparison of the expected sum BEQ (based on the chemical analytical data and the REP values for the individual compounds) and the actual measurements of the total BEQ using the CALUX assays.

Results and Discussion

The results of the chemical analysis show that:

- HCH-isomers are detected in small amounts. Only within the source area high levels are found, with a maximum level of 900 mg/kg dry matter (dm) (sum). The most common HCH-isomer at this location is α -HCH. However, at other locations β -HCH or γ -HCH was most present. Dutch Intervention Values of β -HCH (1.6 mg/kg dm) were exceeded in two cases inside the polygon;

CALUX assay	Biological effect
ER α (estrogen receptor α) CALUX	endocrine disrupting effects by (pseudo)estrogens
AR CALUX (antagonist testing; androgen receptor)	endocrine disrupting effects by anti-androgens
PR CALUX (antagonist testing; progesterin receptor)	endocrine disrupting effects by anti-progestins
AP1 CALUX (AP1-signaling pathway)	effects on cell differentiation, proliferation and apoptosis which relate to carcinogenesis
DR CALUX (AhR receptor)	dioxin(-like) compounds related effects
PAH CALUX (AhR receptor)	(carcinogenic) PAHs-related effects
nrf2 CALUX (nrf2-signaling pathway)	measure for oxidative stress
p53 CALUX (p53-signaling pathway)	measure for genotoxicity

Table 1: CALUX assays included in the research

- Drins (aldrin, endrin, dieldrin) are rarely detected and only in negligible amounts;
 - DDT and its degradation products DDD and DDE are nearly detected in all samples (19 samples out of 21). The highest reported value is 360 mg/kg dm (sum).
 In seven cases inside the polygon and in drain samples, Dutch Intervention Values for (sum) DDT were exceeded (1.7 mg/kg dm).

It is shown that drain and dust samples indicate (still) ongoing off-site migration via surface runoff and wind erosion. A source-path receptor analysis (Witteveen+Bos and Tauw, 2013) shows that exposure of local

people can occur via direct contact, inhalation of contaminated dust, spreading of surface runoff via water bodies, and consumption of contaminated food. The site possesses potential direct risk for trespassers and indirect risk for consumers of meat and dairy products of grazing cattle.

CALUX -results (table 2) show that the samples elicit various responses from the exposed cells in the bioassays.

In general, the two samples taken from inside the polygon areas ('source' and 'gully east') show the highest responses. A decreasing trend in the biological activities going from the source towards

the drains can be observed. Especially the results of the ER α -CALUX are clearly elevated within the source area. The 'gully east' sample shows an activity comparable to 1,75 μ g 17 β -estradiol/kg soil. To our knowledge there are no environmental quality standards (EQS) for compounds based on their estrogenic potency. However, as an indication: For estradiol an EQS of 0.4 ng/l has been proposed for water by the Scientific Committee on Health and Environmental Risks of the European Union (EU, 2011).

Furthermore, activity is measured on the anti-AR, anti-PR and AP1 receptors. In combination with the high stability of

CALUX assay	ER α	anti-AR	anti-PR	AP1	P53	PAH	DR
Reference compound (eq.)	17 β -estradiol	flutamide	Ru486 (mifepristone)	TPA	actinomycinD	benzo[a]pyrene	2,3,7,8-TCDD
Sample name	g/kg ds soil	g/kg ds soil	g/kg ds soil	g/kg ds soil	g/kg ds soil	g/kg ds soil	g/kg ds soil
BW	2,85E-08	8,34E-03	4,30E-06	0,00E+00	0,00E+00	6,84E-05	7,5E-09
Source	1,03E-06	2,50E-01	8,59E-04	1,55E-06	5,49E-05	3,74E-05	9,6E-07
Gully East	1,75E-06	2,50E-01	4,30E-05	0,00E+00	0,00E+00	1,04E-03	5,2E-06
Drain 4	4,12E-08	2,50E-03	1,29E-05	0,00E+00	0,00E+00	1,01E-04	5,6E-07
Drain 5	1,12E-08	2,50E-02	1,29E-04	0,00E+00	0,00E+00	6,83E-05	1,0E-08

Table 2: Absolute results for bioactivity values (BEQ) measured of CALUX assays

the compounds, and depending on the exposure scenario, this indicates a health threat for hormone disruption, developmental disorders, and carcinogenicity. The DR-CALUX and PAH-CALUX assays show low activity, indicating that dioxins, dioxin-like PCBs and PAHs are not a matter of concern. Within the 'gully east' the concentration of PAHs is highest, but only 1 mg BaP/kg soil. For instance, the Intervention Value in the Netherlands is 40 mg BaP/kg. For the p53, activity was only measured from the sample 'source', indicating that except for this location, no genotoxic effects from samples are observed.

In figure 2 (next page), results of the comparison between calculated and measured values (in g/kg BEQ) are presented for ER α -, AR-anti, PR-anti and AP1-CALUX. For the other assays, no comparison could be made due to a lack of chemical data. If the expected BEQs are compared with the measured BEQs it is striking that especially for the sample "source" biological activity could not be predicted from values generated by chemical analysis, except for ER α . Additional toxicity (endocrine disruption and AP1 related activity/carcinogenicity) seems to be present at this spot. For the sample "Gully east", also located inside the burial site, activity on AP1 was predicted but not measured. This relates to

the fact that the expected levels are close to the detection level of this particular assay.

The comparison shows that the mixtures either have unknown compounds that aggravate responses or that individual compounds within the mixture have an enhancing (or in one case, counteracting) effect with regard to toxicity.

Conclusions and Recommendations

The results of both the chemical analysis and the biological, effect-based assay show that, for our case-study, risks are present for both the ecosystem and human health. Even 20 years after the last dumping has taken place, contamination levels are far above the risk-based soil quality standards. Furthermore, substantial toxic effects are measured. Although conclusions on site risks are in essence similar, by effect-based analysis, it is shown that at one particular spot toxicological effects are higher than expected based on chemical analysis of known compounds. Thus, it is indicated that additional toxicity from compounds that were not analysed is present, or that compounds in the mixture pose a synergistic action.

It is concluded that effect-based bioassays are suitable as an alternative and comple-

mentary approach to chemical analysis of the environmental samples for risk characterisation of POPs polluted and hazardous waste dumpsites. To make risk assessment more realistic, as well as more biologically relevant by showing responses on biological effects, it is highly recommended to perform an effect-based analysis. It is especially preferred to use biological effect-based bioassays for risk assessment when:

- chemical analysis do not show clear results, where high levels are expected (an indication that unknown compounds could be present);
 - the pollution is a complex mixture of (known and unknown) compounds that may interact;
 - analysis of individual compounds is either impossible or too expensive.
- The method can be used as a screening without the analysis of individual compounds. Obviously, the predictive value of the effect-based analysis depends on the set of assays that were selected for the assessment. Based on the effect-based analysis, the follow-up analyses may be performed, for example, for chemical analytical identification of the compounds that elicit the adverse effects.

In this investigation, effect-based analysis is successfully used to characterise site risks of samples taken from a dumpsite and its direct surroundings. However, off-site migration and subsequent accumulation of POPs chemicals is more difficult

to embed in a risk assessment, especially when chemicals were dumped decades ago.

Since that time, substantial transport to nearby and large distance sinks (environ-

mental compartments, living organisms and food) has occurred. With current investigation and analysis techniques, the contribution of such a dumpsite to the deterioration of nearby sinks can still not sufficiently be mapped. One way to start

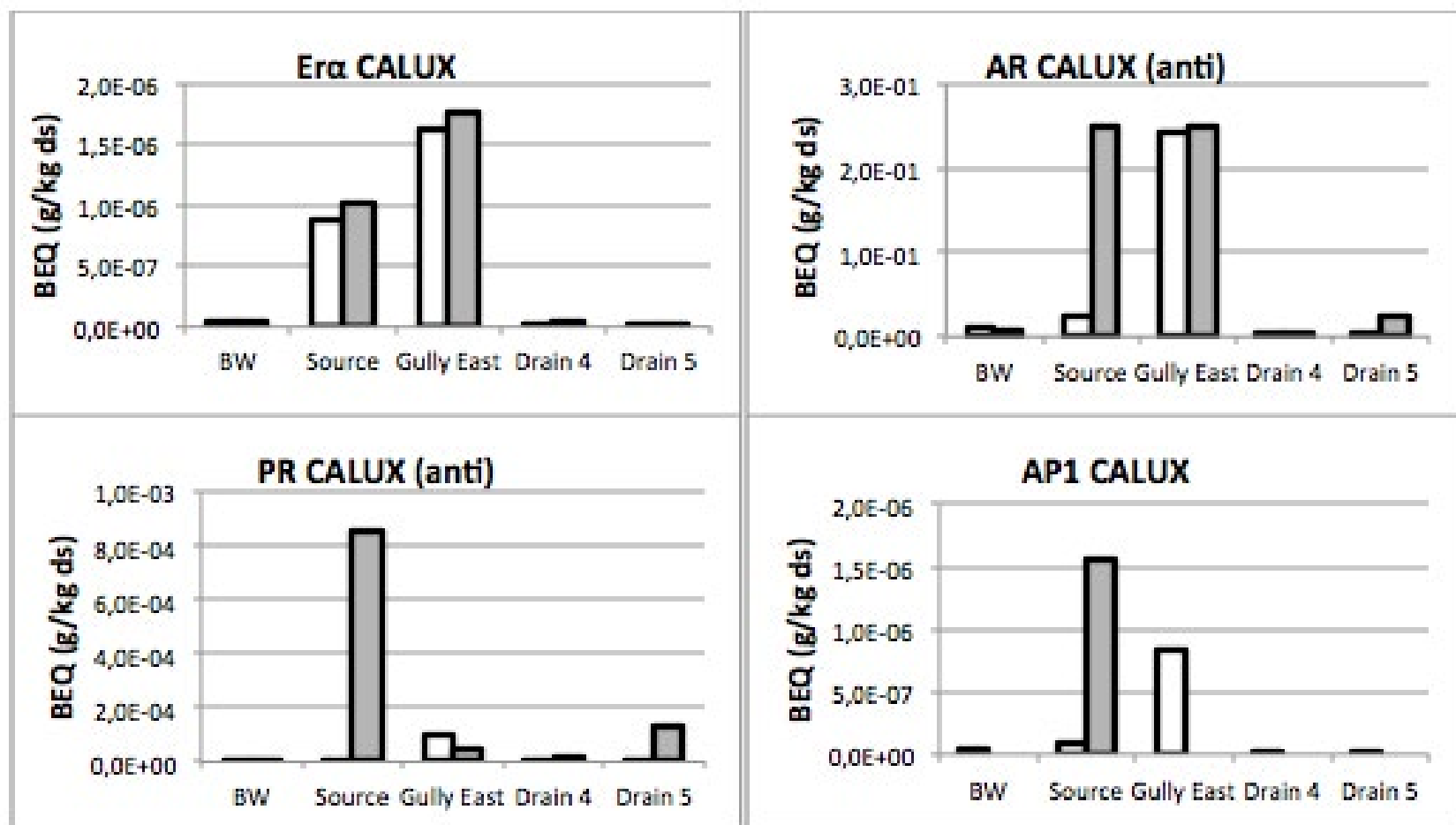


Figure 2: Expected (white bars) versus measured (grey bars) BEQ values of CALUX assays

understanding the impact is to investigate potential sinks that act as human exposure matrices, such as house dust, meat, dairy products and fish. Additionally, biological samples such as blood and mother milk could be analysed. The effect-based analysis of such samples could provide a more realistic risk assessment for human health, taking into account ongoing accumulation and degradation of a POPs dumpsite in the surrounding areas.

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CHARACTERIZATION AND MANAGEMENT OF LINDANE-CONTAINING WASTE AT AN ABANDONED LINDANE PRODUCTION FACILITY IN HUESCA PROVINCE (SPAIN).

PRIMARY EMERGENCY ACTIONS FOR ORGANOPHOSPHATE WASTE CONDITIONING AND EX SITU MANAGEMENT

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Abstract

The remaining raw chemicals and uncontrolled waste after closure of Inquinosa, a lindane-production facility located in the municipality of Sabiñánigo (Huesca, Spain) in 1991 has caused a major concern regarding health and safety conditions and potential environmental risk. Prior to dismantling the plant, the Regional Government of Aragon awarded Adiego Hnos. S.A. the contract to carry out the design of waste characterization and management plans to provide a detailed waste inventory. This included determining the presence of lindane (gamma-hexachlorocyclohexane), setting up appropriate waste management practices and the potential waste disposal alternatives for waste obtained from the site.

During the characterization, samples were taken from bulk materials, out of date

chemicals and the inspection of storage tanks and pools throughout the site. Liquid, sludge and solid substances were sampled and a broad range of lindane-containing waste was identified. Additional potential risk arose from the identification of hazardous chemicals, such as organophosphate compounds with lindane, as well as unstable conditions of waste storage drums and the waste being exposed to atmospheric agents.

As a result, a comprehensive waste inventory was carried out, including waste coding according to current European regulation and a study of alternatives for ex-situ waste management. Site-specific management protocols were developed for individual waste types in order to guarantee maximum compliance with safety standards during handling, conditioning

and transportation. Consecution of the waste management plan included advice to prioritize actions in order to prevent further impact on the environment or to human health due to the potential hazardness of the waste in the current conditions of the site. As a consequence, a primary emergency plan was designed and executed for special conditioning and incineration of waste drums containing O,O-dimethyl hydrogen dithiophosphate with lindane. This waste is corrosive, flammable and toxic for inhalation. Therefore, ATEX equipment, supplied air respirators and special containment drums were necessary.

Keywords

Lindane, Bailín, Inquinosa, Organophosphates, Sardás

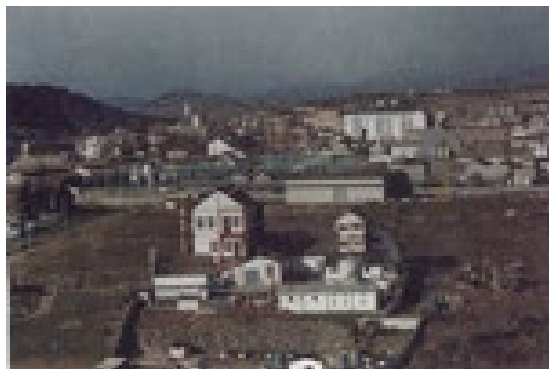
Introduction

The Industrial plant of INQUINOSA is located in the Fosforera Industrial State, next to Sabiñánigo Village. The plant occupies 17,000 m² organized in six units, where buildings occupy 1,200 m² of the total area. The plant was operative between 1974 and 1991. During this period the plant manufactured pesticides and other agrochemical products, mainly lindane (gamma-hexachlorocyclohexane). This activity is currently included in the list of potentially contaminative activities in Spain, as per current legislation (RD9/2005). Production figures from 1989 indicated an annual production of 850 tons of lindane, generating 6,900 tons of hazardous wastes per year (mainly deposited in Sardás and Bailín landfills near Sabiñánigo). The plant is currently closed to the public and controlled by the Regional Government of Aragón (Spain).

In 2012 Adiego was awarded a contract by the Regional Government of Aragón (Spain) to carry out the characterization of the waste products left within the Inquinosa plant facilities and to present a



Figure 1 and 2:
General view and
aerial photo view of
INQUINOSA plant.



Waste Management Plan. The Waste Management Plan takes the list of different waste products from the waste characterization phase and proposes management procedures according to current European and Spanish legislation and techniques for treatment of this hazardous waste.

Methodology

The characterization plan was structured into three main steps: 1) identification and visual inspection of potential wastes; 2) sampling campaign for lab analysis of liquid, solid and slurry substances for lin-

dane confirmation, and 3) preparation of a descriptive sheet for any individual waste encountered in the Plant. Basic information included waste ID, location within the facility, waste description and estimated amount, waste characterization, safety issues, protective measures and feasible management options.

Execution of the characterization plan included 91 samples for laboratory analysis and 59 descriptive sheets. Evaluation and characterization of the waste encountered in the plant showed that 80 % of the waste contained lindane.

Descriptive sheets allowed prioritizing actions regarding wastes of singular concern, considering potential hazardousness of the waste in the current conditions of the site. As a consequence, a work procedure was designed for special conditioning and handling prior to incineration of waste drums containing O,O-dimethyl hydrogen dithiophosphate with lindane .

Large quantities of O,O-dimethyl hydrogen dithiophosphate were discovered within two of the warehouses (25-26). This organic acid is used as an intermediary product in the formation of pesticides. It is classed as corrosive to metals and flammable, it could cause injury to eyes, respiratory tract and skin. It may also

have adverse effects on fertility and the substance is harmful to aquatic organisms. The presence of water hydrolyzes the organophosphate producing highly toxic hydrogen sulfide (H₂S) and heat; therefore extreme caution must be exercised in the case of fire. Furthermore, laboratory analysis confirmed lindane presence. Lindane is a Persistent Organic Pollutant covered under the Stockholm Convention and a possible human carcinogen according US-EPA.

The acid was stored in large 200 L-capacity metallic drums with plastic inner coating. Due to the amount of time that this waste had been stored in the drums, the condition of the recipients had deteriorated significantly (rusted) and in some cases the drums were extremely difficult to handle. The acid found in the interior of the drums had partially solidified and deposited at the bottom of the recipient and showed a liquid layer on top, including an intermediate layer of very viscous substance between them. Nature and hazardousness of the waste and the state of the recipients justified the need for primary emergency actions.



Figure 3 and 4: View of storage drum encountered in warehouses 25 and 26 containing O,O-dimethyl hydrogen dithiophosphate and contaminated with lindane.

Given the nature of the works a Health and Safety plan was necessary, describing additional personal protective equipment (PPE) and other safety measures to be undertaken during the works. In order to reduce employee exposure to hazards when engineering and administrative controls were not feasible or effective to reduce these risks to acceptable levels Tyvek suits with acid protection, chemical-resistant



Figure 5 and 6: Adiego employees with personal protective equipment (PPE). Employees are wearing Tyvek suits with acid protection and respiratory equipment with eye and face protection. Figure 6 shows employee wearing self contained breathing apparatus.

gloves and personal respiratory equipment and eye protection were required.

Adiego's work team was integrated by two field technicians specialized in transfer and conditioning of the drums inside the warehouses and a Project Manager who was responsible for Health and Safety during the works. The working team was complemented by the Facultative Director and an external Health and Safety Manager both from the Regional Government of Aragon.

Transfer and disposal work was carried out during June 2012 as per specifications laid out in the technical guidelines described in the previous Waste Management Plan. The principle objective of the work that was carried out was the preparation and conditioning of the site and the materials necessary for the acid transfer and repackaging as part of the reconditioning protocol. The plan of work included the following specific actions:

- Access routes to the warehouse were cleared and containers (Intermediate Bulk Containers (IBC) and overpack salvage drums) were placed in relevant locations guaranteeing the absence of obstacles that could potentially obstruct or slow down a rapid evacuation of the warehouses in the case of an accident or emergency.

- A security zone was designed in an area between the two warehouses where a washing point was set up. A retention dike was installed as a necessary provision in the case that waste was spilled over workers or machinery. In addition tubular absorbents for corrosive liquids were also installed at the warehouses entry to allow containment of any spillages.

Adiego's work team was integrated by two field technicians specialized in transfer and conditioning of the drums inside

the warehouses and a Project Manager who was responsible for Health and Safety during the works. The working team was complemented by the Facultative Director and an external Health and Safety Manager both from the Regional Government of Aragon.

The procedure of work described in the Waste Management Plan indicated the transfer of the liquid waste to be carried out in-situ when possible, given the indoor location of the waste on concrete surfaces in good condition within the warehouses. The works started in warehouse 25 and were followed in warehouse 26.

Once all Health and Safety measures including personal equipment described in the technical instruction were in order, the specialized field technicians started the transfer and conditioning of the liquid waste, following the next steps:

- Operational check of protective and safety equipment, as well as of proper functioning of machinery. ATEX equipment was compulsory for the pumping device, employing an ATEX compressor for energy supply and an acid resistant double diaphragm pneumatic pump was used to transfer the liquid waste

- Selection of the drum and insert of the

extraction pipe. Transfer of the liquid waste contained in the drum into the IBC. One of the technicians kept one end of the pipe inside the drum and the other checked that the liquid was being transfer into the 1000 L container. In this container, the pipe was held onto the lid of the container to prevent the pipe from accidentally slipping out and causing risk of spillages and splashing. Once the transfer of the liquid was finished in that selected drum, the extracting pipe was extracted from the drum, and the drum was closed with the screw top and marked.

- After all the liquid acid from one container drum was placed in the 1000 L containers and the pumping process was finished, the containers were labeled as "organophosphate acid", placing the pipe inside the next container to continue the transfer works.

- The drums were accumulated in several rows within the warehouse, when the liquid waste from the drums in the first row had been transferred to the container; the drums were repackaged in the individual overpack salvage drums, to be able to assure all safety measures were in place to allow access to the next row.

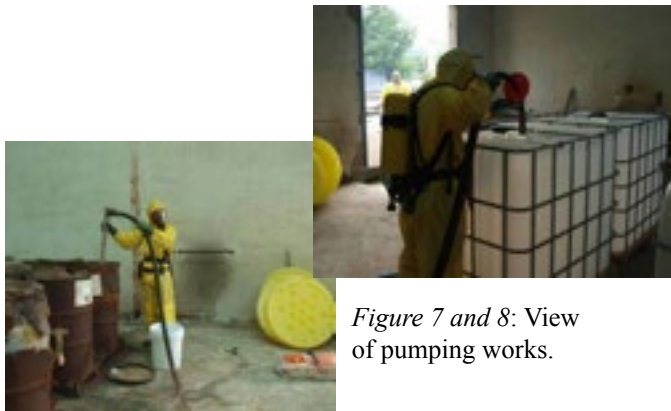


Figure 7 and 8: View of pumping works.

Conditioning and repackaging of the individual drums, including the most viscous and partly solidified acid, into the over-pack salvage drums was done individually by the two technicians. The methodology used for the packaging of the drums inside the overpack was done depending on the state of the drum. If the drum was in an acceptable state the drum was held by two intertwined straps in the upper middle part and lifted by the forklift, then the over-pack salvage drum was slid underneath it, then the drum was lowered carefully and the screw top closed. In the case of severely damaged drums a different methodology was used including manual handling of the drums.

- When the procedure of reconditioning the organophosphate waste was finished in both warehouses the facilities installed for the works were dismantled.



Figure 9 and 10: Repackaging of the drums and liquid waste.



Conclusions

Execution of waste conditioning works resulted in four 1000 L IBC's and 41 over-pack salvage drums, all of them adequately labeled following current legislation. A total of 2,050 L of liquid organophosphate waste containing lindane were transported to Trédi (Sèche Global Solutions) incineration plant near Lyon (France) for destruction.

Specific work procedure for waste conditioning assured a proper and safe execution. Neither personal protection equipment nor any machinery used for the loading of the containers suffered any splashes or spillages, and no emergency actions were necessary.

References

1. Safety Data Sheet Lindane
2. Safety Data Sheet 0,0 Dimethyl Hydrogen Dithiophosphate
3. Spanish Royal Decree 9/2005 14th January
4. Waste and Contaminated Soils Law 22/2011, 28th July (Spanish Boletín Oficial del Estado)

EVALUATION OF SLOVENIAN LAKES FROM 2007 – 2012 – CONTAMINATION WITH SPECIFIC PESTICIDES

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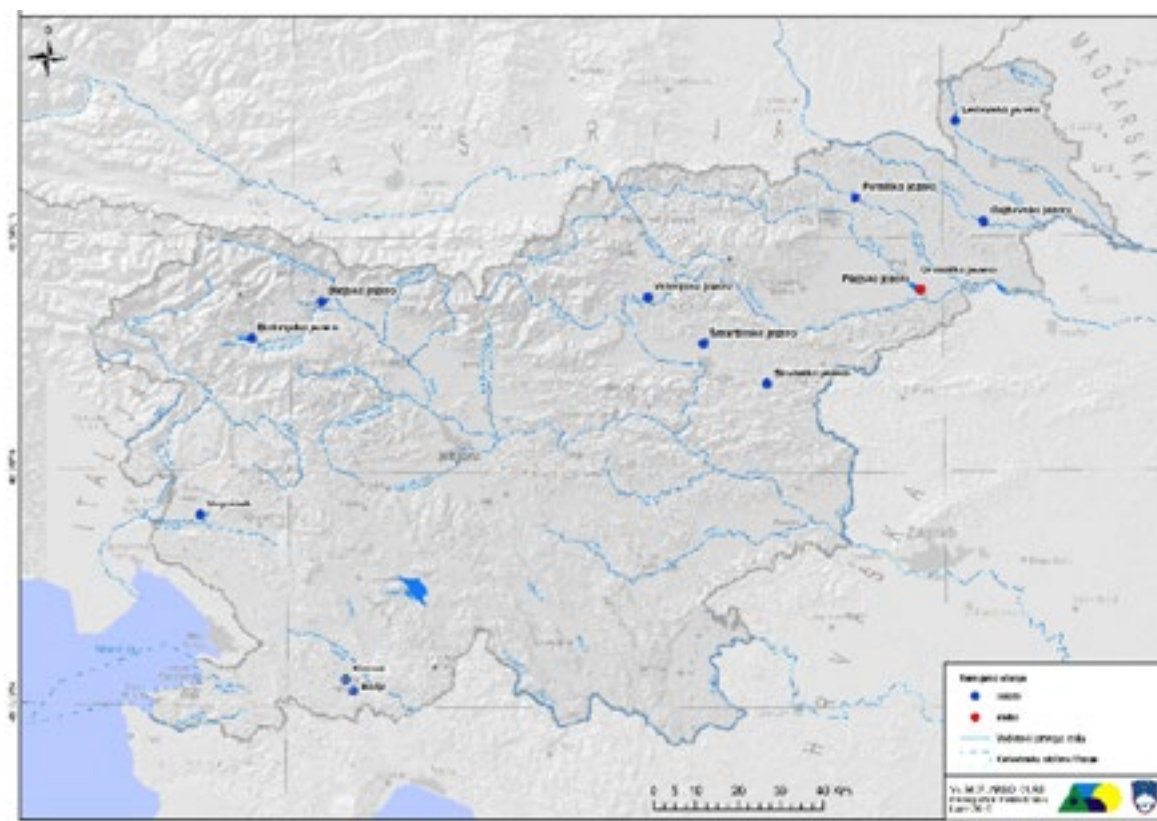
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Introduction

In Slovenia there are 321 bodies of water classified as lakes. Two major ones in the pre-alpine part, Lake Bled and Lake Bohinj, and a number of smaller alpine lakes are tectonically glacial, many are intermittent due to Karst surface, and the rest were formed following dam building on rivers or subsidence due to mining. We evaluated 12 lakes for which the monitoring data were available. Two of them, namely Lakes Bled and Bohinj, are very clean probably due to the fact that there is no agricultural or industrial activity in their immediate surroundings.

Name	Superficies of lakes	Volume	Depth
	km²	m³.10⁶	m
Bled Lake	1.43	25.7	31 max.
Bohinj Lake	3.28	92.5	45 max.
Velenje Lake	1.35	25	55 max.
Smartinsko Lake	1.07	6.5	6 average
Slivnisko Lake	0.84	4	5 average
Pernisko Lake	1.23	3.4	3 average
Ledava Lake	2.18	5.7	3 average
Gajsevsko Lake	0.77	2.6	3 average
Ptuj Lake	3.5	19.8	6 average
Klivnik	0.36	4.3	12 average
Mola	0.68	4.3	6 average
Vogrscek	0.82	8.5	20 max.

Table 1: Basic characteristic of 12 Slovenian lakes



Picture 1: A map of major Slovenian lakes

Monitoring

The national monitoring programme from 2009 onwards was carried out in the bodies of water with surface area above 0.5 km². The following parameters were included: the status of phytoplankton and macrophytes, and general physicochemical parameters and concentrations of plant

protection products (PPP). The samples were taken at the deepest points of included lakes. The frequency of measurements was higher in the north-eastern part of the country in view of the intensive farming and substantial use of PPP. The methods used in the monitoring of Slovenian lakes were selected in 2009 (some parameters for specific lakes from 2007) when most

measurements were carried out. The Lakes Bled and Bohinj were assessed for their integral ecological status.

The following parameters were included:

- plant protection products: alachlor, atrazine, chlorfenvinphos, chlorpyrifos, cyclodiene pesticides (total), DDT (total), diuron, endosulfan, hexachlorobenzene, isoproturon, simazine in trifluralin.
- chemical: cadmium and compounds, lead, mercury, nickel, TOC – total organic carbon, nitrogen (total), ammonia, nitrates, phosphorus (total), SiO₂, nitrites, sulfates, silicon, manganese, iron, aluminium, arsenic, antimony, barium, beryllium, boron, copper, zinc, cobalt, tin, chromium, molybdenum, selenium, vanadium, titanium and around 25 organic compounds.
- biological: phytoplankton, non-vertebrae-benton, macrophytes and phyto-benton.
- other: pH, electric conductance and amount of oxygen.

The sampling for biological analyses was done according to the prescribed methodology [3, 4, 5] and in accordance with the standard procedures and the requirements of the Water Directive (Directive 2000/60/EC).

S: supervisory surveillance

O: operational surveillance

F: phytoplankton

FB+M: phyto-benton and macrophytes

M: macrophytes

BN: non-vertebrae-benton

Ch: chemical parameters for lakes

R: chemical parameters for rivers

HM: heavy metals

TRP: triazine pesticides

TBT: tributyltin compounds

VCH: volatile chlorinated hydrocarbons

Table 2: shows the results of the Slovenian lakes monitoring in 2009

Name	Monitoring	Biological elements	Chemical parameters	Special pollution parameters
Bled Lake	S	F, M	Ch	no registered emissions
Bohinj Lake	S	F, M	Ch	no registered emissions
Velenje Lake	O	F, FB, BN	Ch	HM, Hg
Smartinsko Lake	O	F	Ch	HM-Hg, TRP
Slivnisko Lake	O	F	Ch	HM, TRP
Pernisko Lake	O	F	Ch	HM, TRP
Ledava Lake	O	F	Ch	TRP
Gajsevsko Lake	O	F	Ch	HM, TRP, DFH, AOX
Ptuj Lake	O	F	Ch, R	HM-Hg, TBT, VCH
Kilvnik	O	F	Ch	no registered emissions
Mola	O	F	Ch	no registered emissions
Vogrscek	O	F	Ch	no registered emissions
Druzmirsko lake	O	F	Ch	HM, TRP

In the northeast region triazine pesticides were determined five times during the periods of most intensive use, whereas heavy metals were determined four times. The chemical parameters including heavy metals, volatile chlorinated hydrocarbons and tributyltin compounds were most

frequently analysed in the Ptuj Lake (12 times) due to more polluted influxes. In the rest of the lakes the analyses were less frequent in view of less polluted influxes.

In 2011-2012 of some selected PPP were analysed in all lakes (Tables 3 and 4).

1) Smartinsko Lake 2) Slivnisko Lake 3) Pernisko Lake
4) Ledava Lake 5) Gajsevsko Lake 6) Vogrscsek

YA – yearly average_EQS – ecological quality standards

Active substances and PPP	Unit	YA_EQS	1	2	3	4	5	6
Alachlor	µg/L	0.3	0.008	0.008	0.008	0.008	0.008	0.008
Atrazine	µg/L	0.3	0.002	0.004	0.009	0.009	0.004	0.002
Chlorofenvinphos	µg/L	0.1	0.009	0.009	0.009	0.009	0.009	0.009
Chlorpyriphos	µg/L	0.03	0.003	0.003	0.003	0.003	0.003	0.003
Cyclodiene pesticides-total	µg/L	0.01	0.002	0.002	0.002	0.002	0.002	0.002
DDT-total	µg/L	0.25	0.003	0.003	0.003	0.003	0.003	0.003
Diuron	µg/L	0.2	0.007	0.007	0.007	0.007	0.007	0.007
Endosulfan	µg/L	0.005	0.001	0.001	0.001	0.001	0.001	0.001
Hexachlorobenzene	µg/L	0.01	0.001	0.001	0.001	0.001	0.001	0.001
Isoproturon	µg/L	0.3	0.004	0.004	0.005	0.005	0.004	0.004
Simazine	µg/L	1	0.011	0.011	0.011	0.011	0.012	0.011
Trifluralin	µg/L	0.03	0.001	0.001	0.001	0.001	0.001	0.001

Table 3: Average concentration of PPP in 2011

Active substances and PPP	Unit	YA_EQS	1	2	3	4	5	6
Alachlor	µg/L	0.3	0.008	0.008	0.008	0.008	0.008	0.008
Atrazine	µg/L	0.3	0.002	0.004	0.009	0.009	0.004	0.002
Chlorofenvinphos	µg/L	0.1	0.009	0.009	0.009	0.009	0.009	0.009
Chlorpyriphos	µg/L	0.03	0.003	0.003	0.003	0.003	0.003	0.003
Cyclodiene pesticides-total	µg/L	0.01	0.002	0.002	0.002	0.002	0.002	0.002
DDT-total	µg/L	0.25	0.003	0.003	0.003	0.003	0.003	0.003
Diuron	µg/L	0.2	0.007	0.007	0.007	0.007	0.007	0.007
Endosulfan	µg/L	0.005	0.001	0.001	0.001	0.001	0.001	0.001
Hexachlorobenzene	µg/L	0.01	0.001	0.001	0.001	0.001	0.001	0.001
Isoproturon	µg/L	0.3	0.004	0.004	0.005	0.005	0.004	0.004
Simazine	µg/L	1	0.011	0.011	0.011	0.011	0.012	0.011
Trifluralin	µg/L	0.03	0.001	0.001	0.001	0.001	0.001	0.001

Table 4: Average concentration of PPP in 2012

1) Smartinsko Lake 2) Slivnisko Lake
3) Pernisko Lake 4) Ledava Lake
5) Gajsevsko Lake 6) Vogrscek

YA-yearly average_EQS – ecological
quality standards

Evaluation of the chemical and biological status of the Slovenian lakes

The procedures and requirements for the quality surveillance of the surface waters are covered by the Water Directive (Directive 2000/60/EC). The criteria for the assessment of the chemical and ecological status are determined in the Decree on surface waters status (Official Gazette of the Republic of Slovenia 14/2009).

Table 5 lists the parameters for determining the chemical status. Table 6 lists the biological methods for evaluation of the ecological status, such as phytoplankton, phyto-benton, non-vertebrae-benton and fish.

Number	Parameter	YA_EQS (µg/L)
1	alachlor	0.3
2	anthracene	0.1
3	atrazine	0.6
4	benzene	10
5	bromated diphenylether	0.0005
6	Cadmium and compounds (glede na trdoto vode). Carbon tetrachloride	od 0.08 do 0.15 12
7	Chlorinated alkanes, C ₁₀₋₁₃	0.4
8	chlorofenvinphos	0.1
9	chlorpyriphos (ethyl) cyclodiene pesticides, aldrin, dieldrin, endrin, isodrin. DDT - total	0.03 Σ 0.01 0.025
10	1,2-dichlororethan	10
11	dichloromethan	20
12	di(2-etylhexyl)phtalate-DEHP	1.3
13	diuron	0.2
14	endosulfan	0.005
15	fluoranthene	0,1
16	hexachlorobenzene	0.01
17	hexachlorobutadiene	0.1
18	hexachlorocyclohexane	0.02
19	isoproturon	0,3
20	lead and compounds	7.2

Table 5: Parameters of chemical status with ecological quality standards

21	mercury and compounds	0.05
22	naphthalene	2.4
23	nickel and compounds	20
24	4-nonylphenol	0.3
25	octylphenol (4-(1,1',3,3'-tetramethylbutyl) phenol)	0.1
26	pentachlorobenzene	0.007
27	pentachlorophenol	0.4
28	PAH – polyaromatic hydrocarbons benzo(a)pyrene benzo(b)fluoranthene benzo(k)fluoranthene benzo(g,h,i)perylene indeno(1,2,3-cd)pyrene	/ 0.05 Σ 0.03 Σ 0.002
29	simazine tetrachloroethylene trichloroethylene	1 10 10
30	tributyltin compounds	0.0002
31	trichlorobenzenes	0.4
32	trichloromethan	2.5
33	trifluralin	0.03

Biological elements	Phytoplankton	Phyto-benton	Non-vertebrae-benton
Module*	Trophicity of nutrient burden	Trophicity of nutrient burden	Hydro morphologic changes
No. of sampling sites	1	3	6
No. of samplings/year	4	1	1
Sampling season	Vegetation season	Summer	Summer
Frequency of sampling for WMP	3 consequent years	2/6 years	2/6 years
Parameters for calculations ES	Multimetric index (MMI_PhP)	Trophic index (TI)	Multimetric index (MMI_NVb)
Parameters for calculations	Bio-volume, Brettum index, Chlorophyll (an auxiliary parameter)		Littoral fauna index (LFI), no of taxa, Margefel's diversity index
Evaluation ES for each year	Arithmetic mean of both parameters (4 samplings)	Arithmetic mean of TI of two sampling sites	Weight average MMI_NVb of 6 sampling sites
Evaluation ES for WMP/6 years	Arithmetic mean of MMI_PhP f 3 consecutive years	Arithmetic mean of TI in two years	Arithmetic mean of MMI_NVb in two years

Table 6: Summary of biological methods for evaluation of the ecological status of lakes

WMP - waters management plan

* describing the category of burden the impact of which on the groups of water organisms (biological elements of quality) is evaluated with the selected matrices

Number	Parameter	Unit	Limit values for well status
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Synthetic pollutants

1	1,2,4-trimethylbenzene	µg/L	2
2	1,3,5-trimethylbenzene	µg/L	2
3	bisphenol-A	µg/L	1.6
4	chlorotoluron	µg/L	0.8
5	cyanide (free)	µg/L	1.2
6	dibutyl phthalate	µg/L	10
7	dibutyltin cation	µg/L	0.02
8	epichlorohydrin	µg/L	12
9	fluoride	µg/L	680
10	formaldehyde	µg/L	130
11	glyphosate	µg/L	20
12	hexachloroethane	µg/L	24
13	xylene	µg/L	185
14	linear alkylbenzene sulfonates (C ₁₀₋₁₃)	µg/L	250

15	n-hexane	µg/L	0.2
16	pendimethalin	µg/L	0.3
17	phenol	µg/L	7.7
18	S-metolachlor	µg/L	0.3
19	terbuthylazine	µg/L	0.5
20	toluene	µg/L	74

Non-synthetic pollutants

21	arsenic and compounds	µg/L	7
22	copper and compounds	µg/L	8.2
23	boron and compounds	µg/L	100
24	zinc and compounds	µg/L	100
25	cobalt and compounds	µg/L	0.3
26	chromium and compounds	µg/L	12
27	molybdenum and compounds	µg/L	24

28	antimony and compounds	µg/L	3.2
29	selenium	µg/L	6

Other specific pollutants

30	nitrites	mg NO ₂ /L	/
31	chemical oxygen demand	mg/L O ₂	/
32	sulfates	mg/L SO ₄	150
33	mineral oils	mg/L	0.05
34	adsorbable organic halides (AOX)	µg/L	20
35	polychlorinated biphenyls (PCBs)	µg/L	0.01

Table 7: Limit values of specific pollutants in surface waters according to the Decree on surface waters status

In 2012, the chemical status based on the pollutants listed in Table 7 was determined 12 times in the Ptuj Lake and the Smar-tinsko Lake. The annual average as well as the highest concentration of tributyltin compounds was exceeded in the Ptuj Lake. In the Velenje Lake mercury was also determined four times besides other

heavy metals; these did not exceed the ecological quality standards.

Lake	Confidence limits	Cases of sampling frequency in 2012	Status 2010	Stabdard of confidence
Lake Bled	High	no emission	good	high
Lake Bohinj	High	no emission	good	high
Lake Ptuj	High	12	bad	high
Velenje lake	Medium	4	good	medium
Smartinsko lake	Medium	12	good	high
Slivnisko lake	Medium	4	good	high
Pernisko lake	Medium	12	good	high
Gajsevsko lake	Medium	4	good	high
Ledava lake	Medium	4	good	high
Ormoz lake	Medium	no emission	bad	high

Table 8: Chemical Status of Slovenian lakes in 2010

Confidence limits of chemical status were high in cases of sampling frequency 12 per year; medium in cases of sampling frequency lower than 12 per year; low when there were no monitoring data , but only evidence of emissions.



The Bled Lake

In the Bled Lake 4 samplings to determine physicochemical parameters and phytoplankton were done in the depth vertical in 2010, whereas in 2009 the status of the macrophytes was also assessed.

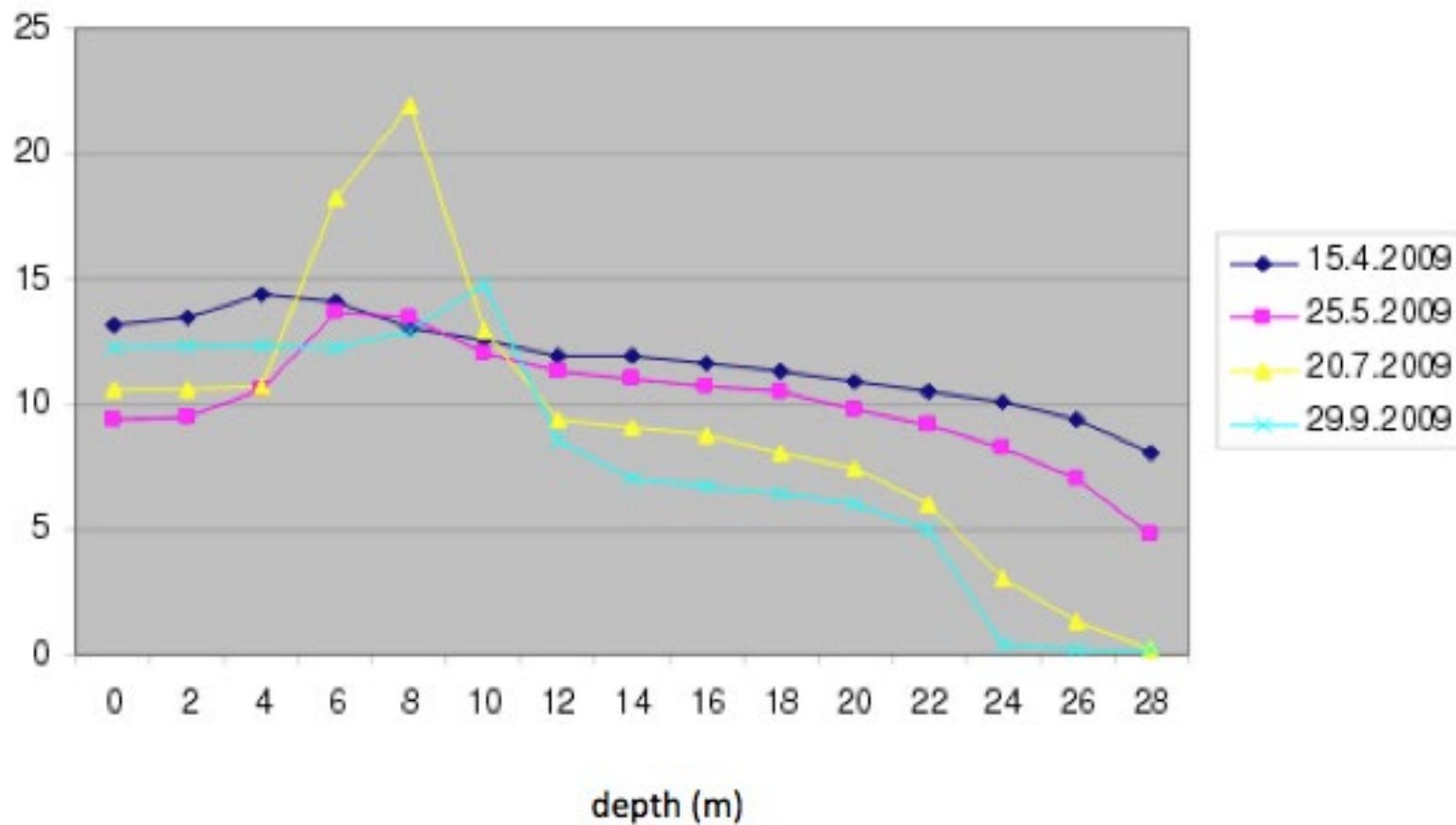
Picture 2: A photograph of the Bled Lake

Parameter	Measured average value	Including in calculation	Brettum - index
		%	Absolutely
Biovolume (mm^3L^{-1})	2.20	61 %	1.35
Abundanca (number of cells L^{-1})	6346	76 %	4830
Total number of identified species	42	50 %	21

Table 9: Some parameter standards in the Bled Lake

Diagram 1: Concentration of oxygen in the Bled Lake in 2009

Concentration of oxygen (mgO_2/L)



The moderate status of phytoplankton suggests, that the Bled Lake is overburdened with the nutrients.

Yearly average concentration	2007	2008	2009
Phosphorus (total) (µg/L)	12.7	11.0	13.2
Inorganic nitrogen sources (µg/L)	350	350	422
Chlorophyll (µg/L)	2.7	3.9	3.7
Transparency (m)	8.3	6.6	5.0

Table 10: General parameters for eutrophication and chlorophyll in the Bled Lake from 2007 - 2009

In 2009 the average concentration of phosphorus and nitrogen compounds was increased in the Bled Lake. Of particular concern was the average annual concentration of phosphorus which should be below 8 µg/L in the deep alpine and pre-alpine lakes.

The Bohinj Lake

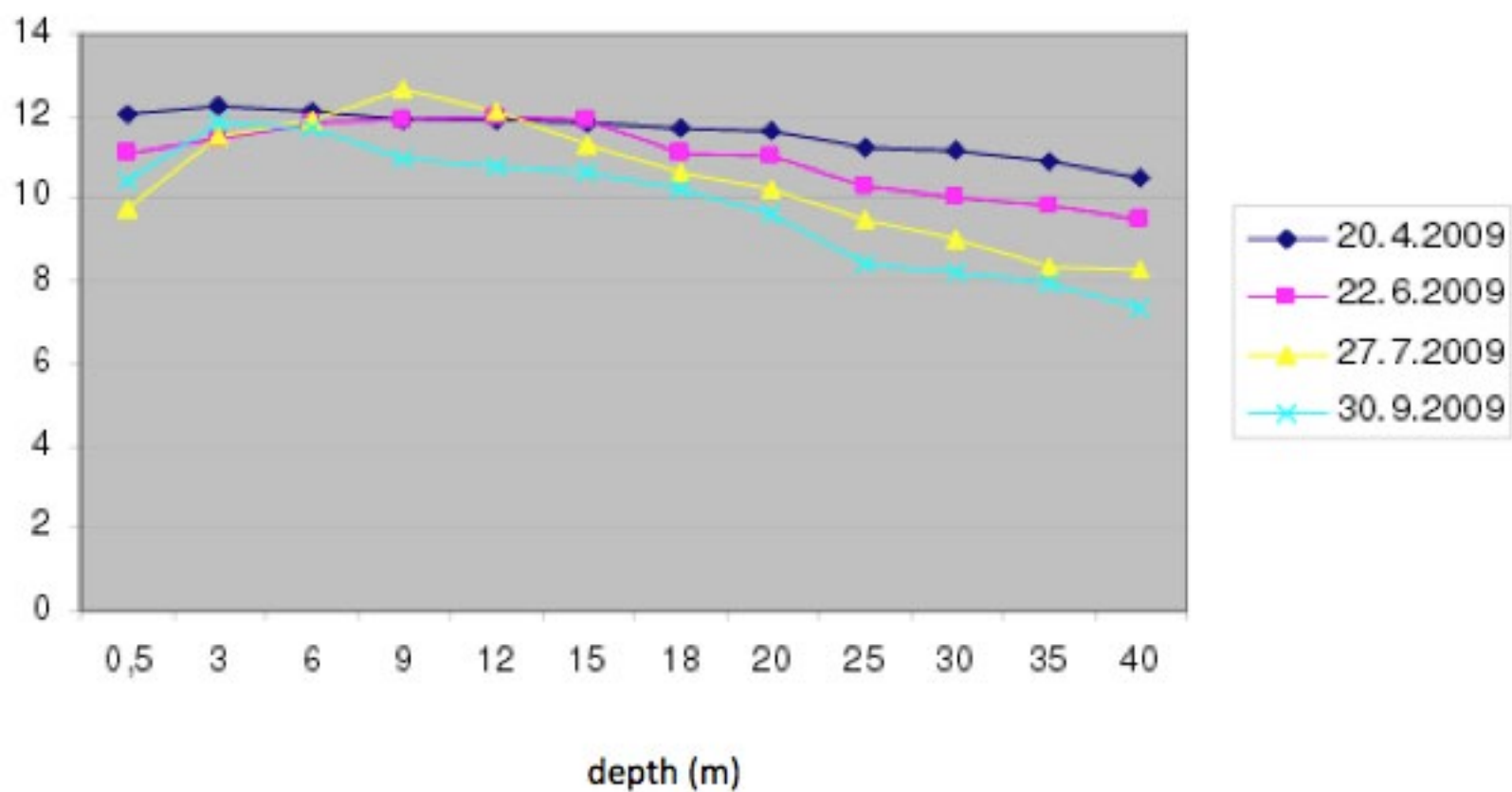
As in the Bled lake 4 samplings were done in the Bohinj lake in 2010.



Picture 3: A photograph of the Bohinj Lake

Diagram 2: Concentration of oxygen in the Bohinj Lake in 2009

Concentration of oxygen (mgO_2/L)



Yearly average concentration	2007	2008	2009
Phosphorus (total) ($\mu\text{g/L}$)	5.2	3.6	3.5
Inorganic nitrogen sources ($\mu\text{g/L}$)	512	454	394
Chlorophyll ($\mu\text{g/L}$)	1.0	1.0	1.2
Transparency (m)	9.2	9.0	8.3

Table 11: General parameters for eutrophication and chlorophyll in the Bohinj Lake from 2007 - 2009

The comparison of the data in Tables 10 and 11 based on the criteria and static analyses suggests, that the Bohinj Lake can be classified as ultra-oligotrophic lake, and that much cleaner than the Bled Lake.

The Velenje Lake

The Velenje Lake is an artificial lake in which 4 sampling were performed in 2009; the analyses were the same is in the Bled and Bohinj Lakes.

The concentrations of oxygen from the depth of 15 m were less than $1 \mu\text{g/L}$ thus indicating that the majority of the water mass was without oxygen throughout the year.

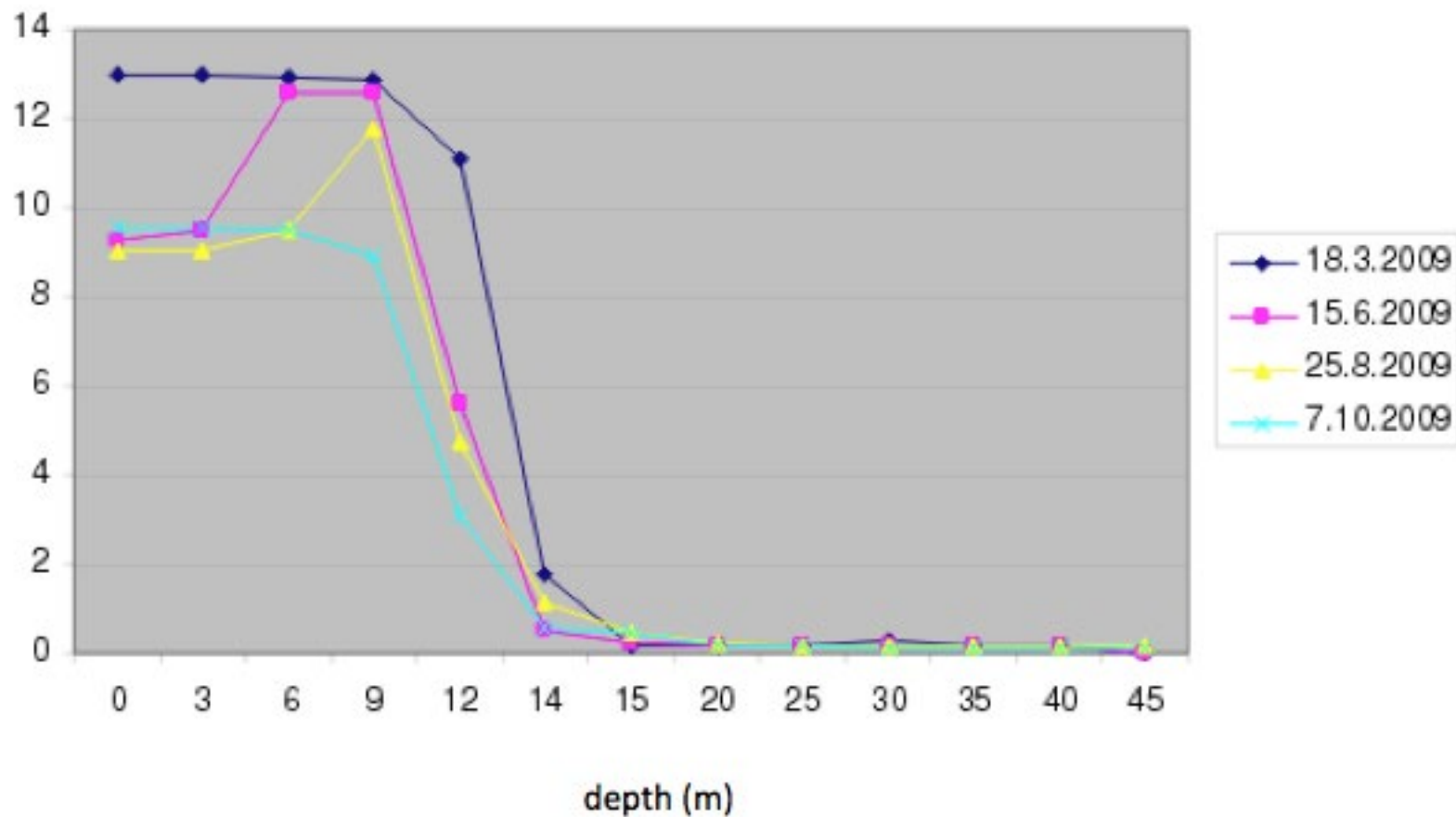


Picture 4: A photograph of the Velenje Lake

There are anaerobic degradation processes in the lake resulting in high concentration of hydrogen sulphide (H_2S).

Diagram 3: Concentrations of oxygen in the Velenje Lake in 2009

Concentration of oxygen (mgO_2/L)



There are a steam power station and a lignite mine in the immediate vicinity of the Velenje Lake which are the sources of the increased amounts sulphates, molybde-

num and cobalt in the lake. The legally set limits were exceeded up to ten times (see Table 12).

Specific pollutants	Sulfates			Cobalt (filtrate)			Molybdenum (filtrate)		
	mg/L			µg/L			µg/L		
YA_EQS	150			0,3			24		
Year	2007	2008	2009	2007	2008	2009	2007	2008	2009
Velenje Lake	718	613	563	/	0.3	0.3	243	213	165
Sampling frequency	26	10	10	4	12	4	4	12	4

Table 12: Specific pollutants in the Velenje lake from 2007-2009

Yearly average concentration	2008	2009
Phosphorus (total) µgP/L	30.4	24.5
Inorganic nitrogen sources (µg/L)	766	1433
Chlorophyll µg/L	3.3	2.6
Transparency m	4.6	6.8

Table 13: General parameters for eutrophication and chlorophyll in the Velenje Lake from 2008 - 2009

In comparison with Lakes Bled and Bohinj, the Velenje Lake is highly degraded.

We believe that much effort and substantial financial resources would be required to remediate the situation.

Other Lakes

The triazine pesticides, metolachlor and terbutylazin, total phosphorus and anorganic nitrogen were analysed five times per year in the other Slovenian lakes in the north-eastern region. The Gajsevsko and the Pernisko lakes were overburdened with pesticides. The concentration of metolachlor in June 2008 and 2009 were 3.2 and 3.7 µg/L, respectively in the Gajsevsko Lake (one of the smaller Slovenian lakes) whereas the yearly average were 9 and 1.5µg/L, respectively. Terbutylazine was also exceeded in this lake.

In the Pernisko Lake the average concentration of the chlorophyll, phytoplankton bio-volume and phosphorus was high. These data suggests that the Pernisko Lake was most burdened with nutrients and eutrophication followed by the Lendavsko, Gajsevsko and Smartinsko Lakes (see Table 15) resulting in the decline of wildlife in these lakes.

Extra pollutants	Metolachlor		Terbutylazin	
	µg/L		µg/L	
YA_EQS	0,3		0,5	
Lake/Year	2008	2009	2008	2009
Smartinsko Lake	0.4	0.04	0.1	0.03
Slivnisko Lake	0.2	0.1	0.1	0.04
Pernisko Lake	0.3	0.3	0.1	0.2
Ledava Lake	0.6	0.2	0.2	0.2
Gajsevsko Lake	0.9	1.5	0.5	0.8

Table 14: Concentrations of specific pollutants in other lakes from 2008-2009

Parameter	Phosphorus (total) µgP/L	Inorganic nitrogen sources (µg/L)	Phosphorus (total) µgP/L	Inorganic nitrogen sources (µg/L)
	Average 2008	Average 2008	Average 2009	Average 2009
Unit	µg P/L	µg N/L	µg P/L	µg N/L
Smartinsko Lake	49	708	160	494
Slivnisko Lake	29	859	37	533
Pernisko Lake	126	893	252	470
Ledava Lake	104	913	137	1018
Gajsevsko Lake	89	890	122	804
Ptujsko Lake	59	1187	35	898
Klivnik	10	827	15	661
Molja	14	525	15	529
Vogrscek	9	756	10	626

Table 15: Average annual concentrations of total phosphorus and inorganic nitrogen in other Slovenian Lakes from 2008-2009

Conclusion

In 2011 sulphates, phosphorus and inorganic nitrogen were exceeded in six lakes. These lakes did not reach a satisfactory ecological status; in some of them certain pesticides were also exceeded.

The monitoring results in 2012 showed deterioration in seven lakes including the Bled Lake which used to be judged as clean. In the Bled lake pesticides were not detected, however there was a lack of oxygen. The biological surveillance revealed best results for the Bohinj and Bled Lakes. These two Lakes are in the pre-alpine region and are the cleanest among the Slovenian major lakes.

Overburdening with the specific pollutants was noted in the Velenje Lake, the Perniški and the Druzmirski Lake. Metolachlor was exceeded in the Pernisko, Lendava, Slivnisko and Gajsevsko Lake. In the Gajsevsko Lake the concentration of terbutylazine was also exceeded. These data indicate the continuous use of PPP, particularly in the agriculturally developed northeastern region of Slovenia. However the obsolete organochlorine pesticides were found at very low levels which indicate that further monitoring of these pesticides may not be justified on the annual basis.

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INVENTORY OF POP PESTICIDES POLLUTED AREAS IN MOLDOVA

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Abstract

The objective of this study was to identify the POPs polluted areas posing the highest environmental and health risks as well as mapping of those areas using the GIS tool.

An original methodology of POPs pollution study and hazards assessment was developed aiming at: (i) identification and assessment of potentially POPs contaminated sites all over the country; (ii) creation and filling of the POPs database as well as mapping and visualization of acquired data; and (iii) setting the reporting formats and assuring the database support.

All identified potentially contaminated sites were described based on a unified question-naire; the coordinates of the POPs sites were determined using GPS; photo images and composite soil samples were taken at each site. The soil samples were further analyzed for POPs in a certified laboratory. About 1600 contaminated sites were identified and described.

An integrated GIS system for POPs data mapping and analysis was developed allowing storing effectively, managing and presenting POPs information such as geographic locations of the sites, concentrations and other related parameters as well as distribution of health and environmental hazards. The database is available on the Ministry of Environment website: <http://pops.mediugov.md>. The information on POPs polluted sites is to be periodically updated by the environmental authorities.

With the POPs database, the central and local authorities got a new tool which could significantly improve the management of contaminated sites. It can effectively support the policy and decision making process in the field of contaminated sites management.

Keywords

Persistent organic pollutants (POPs), contaminated sites, database, risk assessment.

Introduction

The decades of intensive use of pesticides in Moldovan agriculture left behind many hundreds of sites polluted with POP pesticides (emptied storage facilities, former blending stations, pesticides filling sites, equipment washing platforms, obsolete pesticides dumps, etc.). At the beginning of this study, the available information on their exact location, status and – most importantly – associated risks was scarce. This did not allow for setting priorities, selecting proper management options and policy planning.

The overall objective of this study was to identify the POPs polluted areas posing the highest environmental and health risks as well as mapping those areas using the

GIS tool. Within this overall objective, the more specific objectives were as follows:

- development of the methodology of the POPs pollution study and risk assessment;
- design of the POPs contaminated areas database;
- development of the sampling program and field trial;
- analyses of POPs contents in the collected samples;
- creating the database and mapping POPs polluted areas using the GIS technology;
- identification of environmental and health risks zones.

The assignment was conducted within the GEF/WB POPs Stockpiles Management and Destruction Project, during the period of 2008-2010 years by the Center for Strategic Environmental Studies ECOS in cooperation with Trimetrica SRL, and managed by POPs Sustainable Management Office (www.moldovapops.md).

Approaches

The problem of POPs contaminated sites in Moldova represents the legacy of at least half a century of intensive agriculture and industrial development complicated by the radical change of social and economic model undergone by the country in the 1990s. While starting the study, the

information on potentially contaminated sites was either unknown or incomplete. Many of such sites have been abandoned and forgotten, and only the minority has previously been described and assessed in terms of health and environmental risks. Moreover, most existing data were inaccessible or unusable because of being scattered between different institutions (or different levels of the same institution) and existing only on paper. Besides, there was a problem of data ownership since the responsibilities in this field were not always clear.

Bearing all this in mind, the study was structured around three main elements: (i) identification and assessment of sites potentially contaminated with POPs over the country; (ii) creation and filling of the POPs database as well as mapping and visualization of acquired data; and (iii) setting the Reporting Formats and assuring the database support and training, required for further renewal and operation of the POPs database.

Identification and assessment of sites potentially contaminated with POP

To ensure the most effective and complete way to identify the potentially contaminated sites, it was decided to gather the information at the local level rather than use

the data available at the central level. The information was basically collected from two sources: the mayoralities and local operators. Official letters were sent to all rural and urban mayoralities (898 in total) asking, on map, to indicate the location of former facilities related to pesticides use. In parallel, local operators with relevant knowledge and professional experience were hired to complete the task.

The information collected from the mayoralities was used as a starting point for further field investigation. The field teams visited and described all identified potentially contaminated sites, based on a unified questionnaire; determined the coordinates of the POPs sites using GPS devices; took photo images and composite soil samples at each site. The soil samples were further analyzed for POPs in a certified laboratory.

The field operators were thoroughly trained and worked in accordance with the developed standard procedures in order to assure the quality and completeness of the work done. The information obtained was processed and incorporated into the database.

The general approach to assessing the hazards associated with the sites potentially contaminated with obsolete pesticides

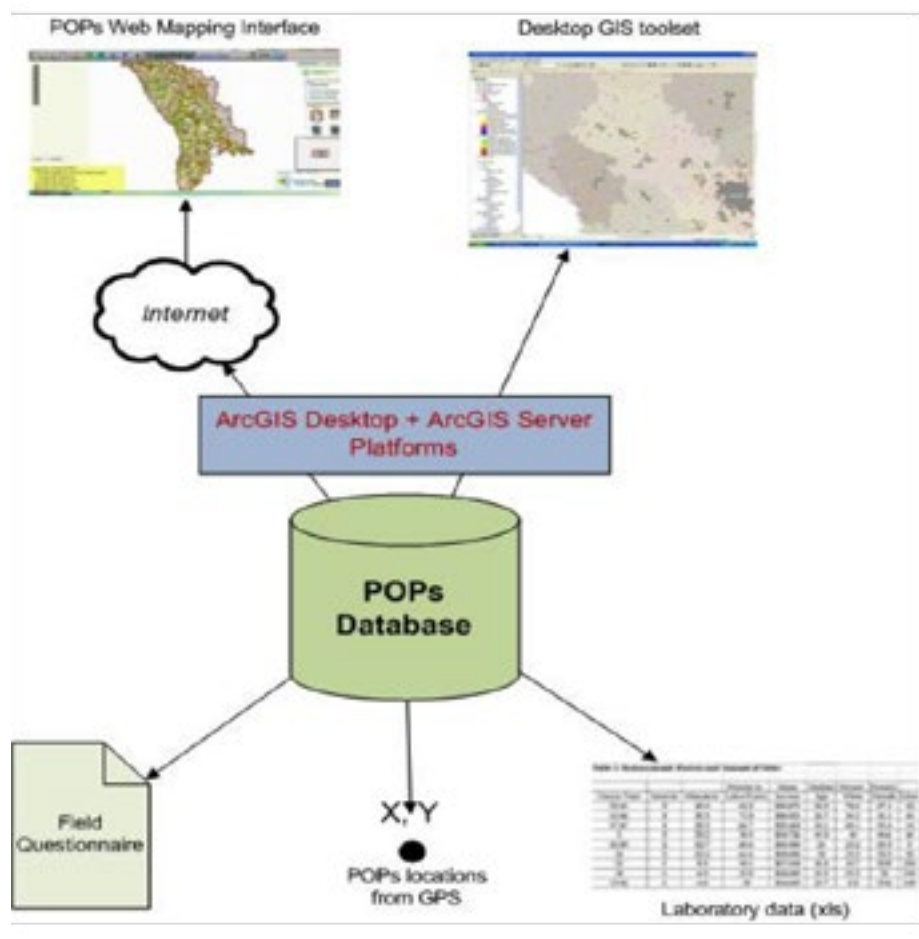


Figure 1: Scheme of the integrated GIS system for POPs data mapping and analysis

(POPs residuals, in particular) included the following: (i) gaining the information on-site concerning the status of pollution

POPs environmental pollution database
A POPs environmental pollution database has been developed in order to ensure a structured management of POPs information to support the effective decision

sources, the nearest risk receptors and the potential for contamination spreading; (ii) establishing the degree of environmental pollution with POPs; (iii) integration of the data gathered on-site with relevant digital map layers, information from topographical maps, aero-photo images; and (iv) calculation of “hazard indexes”.
/1/

making process at the Ministry of Environment.

The proposed integrated GIS system for POPs data mapping and analysis (Figure 1) allows to effectively store, manage and present POPs information such as geographic locations of the POPs sites, concentrations and other related parameters as well as distribution of health and environmental hazards (<http://pops.mediu.gov.md>).

The POPs Database and its fields were designed in a way to allow database structure scalability, i.e. the ability to make changes in existing configuration and add more data sets later on. Moreover, the database allows smooth compatibility with any standardized databases defined for integration into the Information Management and Reporting System (IM&RS).

All data acquired during contaminated sites investigation were entered into the POPs Database. The data incorporated into the database were fully based on the Reporting Format requirements (the field questionnaire completed by the operators on-site). At the same time, the data on POPs sites included in the database are linked with other types of information obtained in the field. The site’s unique code was used for linking all available information per POPs site.

Reporting Format

The information on POPs polluted sites needs to be periodically updated, most probably, by the district ecological inspectors. This information should be transferred, processed and stored at the Ministry of Environment in order to be used in the decision-making process. A precondition for efficient use of data at the central level is to have a homogenous and standardized dataset coming from the local sources. To secure such uniformity of data a special Reporting Format is to be used by the district inspectors.

The Reporting Format was regarded as a uniform platform for sites assessment. In this sense, it consists of the following elements: (i) coordinates of the site; (ii) the field questionnaire, to be filled during site investigation; (iii) technical instructions treating in detail the field operations; (iv) photo and sampling protocols; (v) laboratory standard form; and (vi) procedures for collecting, transferring, checking data and filling the database. /1/

Inventory Findings

Distribution of sites potentially contaminated with POPs. Altogether, 1588 sites potentially contaminated with POP pesticides and 16 sites contaminated with PCB were identified and described. The terri-

torial distribution of POPs sites averaged by districts is presented in Figure 2. The national average figure is 0.05 sites/km² or one site per 20 km².

Pesticide related infrastructure. During the inventory, a variety of potentially contaminated sites were identified: different types, small and large, simple and complex. In many cases, the old pesticide sites were designed and used for more than one purpose: for example, storage facilities together with blending stations and evaporation grounds; or blending stations with helicopter platform nearby. Altogether, the 1588 investigated sites hosted 2326 major pesticide related infrastructure elements: storehouses, blending stations, helicopter platforms, evaporation reservoirs, as well as illegal pesticide dumps.

Technical condition of major installations found at the POPs sites.

The technical condition of the major pesticide related infrastructure found at the investigated sites was generally poor what contributes significantly to increased environmental risk generated by the contaminated sites. While considering infrastructure engineered and built in the past, less than 9% from the total number of constructions (200 objects) were found undamaged, and those were only storehouses. /1/

Degree of POPs Contamination of sites

In total, 1651 samples from investigated sites were analyzed by the laboratory, including 1590 soil samples. Besides composite soil samples (as defined above), waste samples were taken from the debris found at some old storage facilities. Those usually represented a mixture of obsolete chemicals with construction rubble and soil. The information about their pollution level and spectrum was used for the evaluation of additional risks for the environmental and public health.

Level of soil contamination with POPs pesticides. The range of POPs pesticides analyzed in composite soil samples included the substances specified in the text of the Stockholm Convention on POPs (2001), namely aldrin, dieldrin, endrin, chlordane, DDT (six metabolites), hexachlorobenzene, heptachlor, mirex, and toxaphene, as well as hexachlorocyclohexane (three isomers).

Five POPs (groups of) compounds namely Σ DDT, Σ HCH, chlordane, heptachlor and toxaphene have been found in soil samples taken at investigated sites, in concentrations exceeding the national standard for organochlorinated substances in soil (0.1 mg/kg).

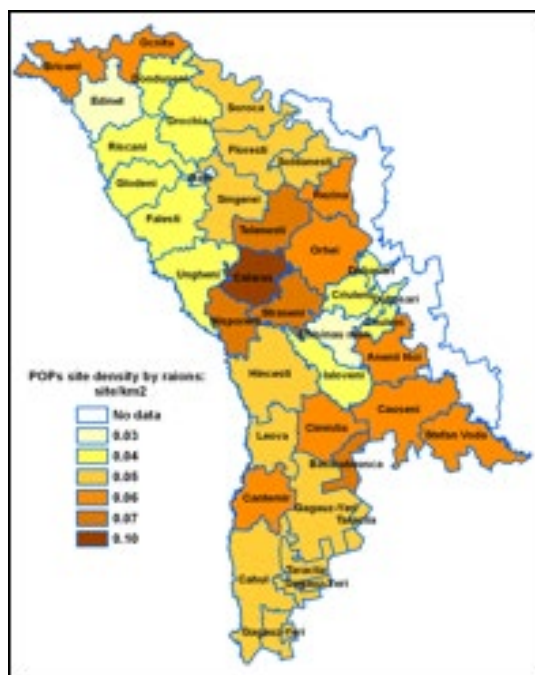


Figure 2: Territorial distribution of POPs sites by districts

The pollution of POPs sites with DDT and – to lesser a extent – with HCH can be defined as widespread. The share of sites contaminated with chlordane (31%) and heptachlor (22%) is also significant. Fewer sites are polluted with toxaphene (about 10%), but, very often, this is a severe level of pollution. Aldrine, dieldrine, endrine, HCB and mirex were not detected in the investigated samples.

The acquired data showed a severe level

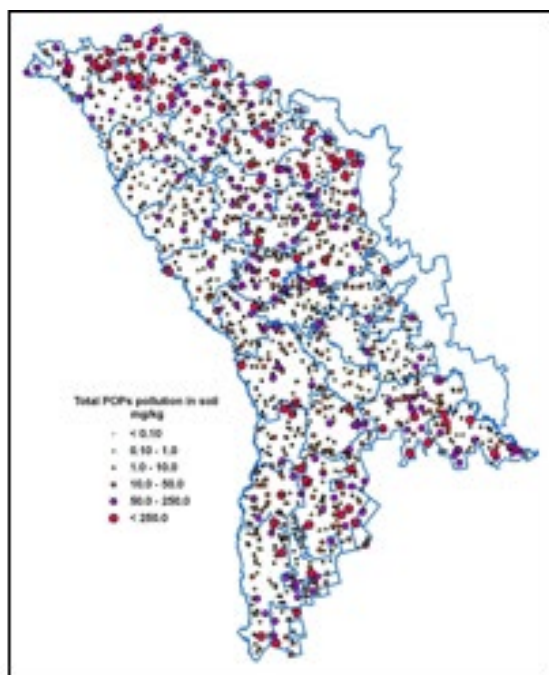


Figure 3: Spatial distribution of contaminated sites

of soil contamination with POPs pesticides at some investigated sites, in the order of hundreds and even thousands of mg/kg. Many of the sites have been polluted by several POPs compounds, which pose the problem of potential synergistic effects on the humans and the natural environment. The pesticide construction waste samples on 42 sites. They showed a high level of contamination and have an irregular statistical distribution.

Spatial distribution of POPs polluted sites. The spatial distribution of investigated sites polluted by POPs is presented in Figure 3. The data are expressed as the sum of all POPs detected on-site in composite soil samples. 252 sites (about 16% of the total number) showed concentrations exceeding 50 mg/kg. At this level of pollution, the soil can be classified as hazardous waste. For these sites, the measures preventing the access of and contact with the population as well as remediation measures to minimize the pollution spreading are to be envisaged.

It must be mentioned that 18 administrative units have a higher prevalence of severely polluted sites (> 50 mg/kg) as compared to the average national value of 16% from the total number of sites. Most often, the pollution mix at those sites consisted of DDT metabolites, HCH isomers and toxaphene.

Prioritizing of POPs contaminations sites

To protect human and ecosystems health, it is becoming common to remediate contaminated sites. However, the great costs associated with it make it crucial to pinpoint those sites that are in greatest need of remediation.

The POPs sites hazard assessment

Besides the data on sites location, assessment of pesticide infrastructure condition, level of soil pollution on site, etc., the database users get the so-called Site Hazard Total Score (SHTS) associated with every contaminated site. The SHTS provides the numeric expression of the danger which the site is posing to human health and environment. The sites are classified/ranked by SHTS from extremely dangerous to low dangerous ones.

The assessment of contaminated sites is an important precondition for ranking them in view of developing site specific remediation strategies. At the study moment, Moldova did not have formal requirements for contaminated sites assessment. Under

this assignment a hazard assessment methodology for POPs contaminated sites was developed and tested. The methodology forms the basis for a developed POPs database computerized module calculating the respective risk indexes and SHTS and for respective ranking of sites by their hazards. /1/

The Site Hazard Total Score is used for ranking the site hazard according to the five generic groups. According to this ranking scheme, the full set of investigated POPs sites were prioritized as follows:

The Beneficiary may decide to apply a different way for sites prioritization, e.g. making a priority list basing on Risk Receptors sub-index only, or using the

sum of POPs concentrations as a criterion for priority setting. The developed Integrated POPs Information System is flexible enough and capable of using both pre-settled and modified algorithms. Such modifications can be done by the database administrator, by intervening in the calculation programme.

The approach to address site contamination

The ranking system based on Site Hazard Total Score itself does not and cannot serve as an ultimate management tool so that necessary measures are taken to ensure that environmental site management initiatives are implemented in timely and cost-effective manner. The Site Hazard Total Score is the only one – probably the

Site Hazard Total Score (as percentile value, based on the statistical data set)	Site hazard rank	Site priority for remediation strategy	Action needs	Number of contaminated sites	
> 95 %	I	Very high	Urgent	76	4.8 %
65 – 95 %	II	High	In short-term perspective	467	29.7 %
35 – 65 %	III	Medium	In medium-term perspective	513	32.7 %
5 – 35 %	IV	Low	In long-term perspective	440	28,0 %
< 5 %	V	Negligible	General protective / low cost measures required	76	4.8 %

most important – but still one among some other parameters which should be considered before the decision to act (clean-up measures, reducing risks measures) is taken. The ranking system proposed is extremely important when assessing a large number of POPs polluted sites in order to set priorities for further decision making process regarding sites remediation.

A step by step approach to address the site pollution is provided as recommendation for further actions. It is inspired by the way of how the issue is addressed in Canada /2/ and envisages the sites where urgent and short-term perspective measures are required.

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CLASSIFICATION OF POPS PESTICIDE DUMPSITES

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This session was used to present and demonstrate the use of a simple classification tool. This tool is developed to present a holistic view on the status of a POP pesticides dumpsite, to explain the current status of a site and facilitate the identification of the gap(s) to break the infinite site assessment circle (Joop Harmsen et al., 2009) and to sustainably manage the dumpsite.

The introduction of this session was given by Boudewijn Fokke (Tauw, the Netherlands). The fact that the status of a dumpsite can vary from uncontrolled to controlled and the dumpsite characteristics describing the status were discussed. The chosen dumpsite characteristics are environmental risks, awareness of stakeholders, the availability of funds for sustainable site management, and availability of site remediation techniques.

The next part of the session was used to demonstrate the application of the tool. The first case was presented by Ingrid Rijk

(Witteveen+Bos, the Netherlands). She used the tool to demonstrate the development of the 100 hectare hazardous waste dumpsite of Volgermeer the Netherlands from an uncontrolled to a completely controlled site over the last 60 years.

Tomasz Stobiecki (Institute of Plant Protection, National Research Institute Sosnicowice Branch, Poland) gave a presentation on the status of the Rudna Góra, a POPs pesticide dumpsite near Jarworzno in Poland, over the last 100 years. Matthijs Bouwknecht and Boudewijn Fokke (Tauw, the Netherlands) characterized respectively the POPs pesticide dumpsite Suzak A in Kyrgyzstan and the Nubarashen dumpsite in Armenia. The last presentation of the session was by Joop Harmsen (Alterra Wageningen, the Netherlands) on his experiences in the 'Risk Reduction of Soil Contaminated by Obsolete Pesticides in Africa' project.

After the presentations of the cases, the usefulness of the tool was discussed with

the audience. It was concluded that POPs pesticide dumpsite classification demonstrates which initiatives should be taken to arrive at a sustainable dumpsite management. It was also concluded that the tool should be improved by including the legal status of the site and the willingness to allocate funds for sustainable site management.



NEWLY LISTED POPS AND OTHER STOCKHOLM CONVENTION ISSUES



THE STOCKHOLM CONVENTION NATIONAL IMPLEMENTATION PLAN UPDATE – THE APPROACH OF ROMANIA

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Abstract

Facing the same problems as other countries in relation to POPs, Romania decided to join the global agreement and ratified the Stockholm Convention in 2004 by Law no 261. After ratification the next step was the development of its first National Implementation Plan (NIP), with financial support from GEF and technical assistance from UNIDO. The NIP was adopted by the Minister in April 2006 and sent to the Stockholm Convention Secretariat.

Romania as a member state of the European Union (EU) and a party to the Stockholm Convention and has the obligation to fulfill its commitments related to the implementation of the convention.

The obligations on implementation of the convention are introduced into European law through Regulation (EC) No. 850/2004 on POPs. Pursuant to Article 7, paragraph 1, i. (c) of the Stockholm Convention and Article 8 (4) of Regulation (EC) No. 850/2004 on POPs Romania is

obliged to review and update its NIP after inclusion of new POPs in the Annexes to the Convention.

In national legislation the measures on implementation of Regulation (EC) No. 850/2004 on POPs are regulated by Governmental Decision no 561/2008. Legal ground for the implementation of the NIP is the Governmental Decision no 1497/2008.

It is important to mention that the Member States have to comply with the EU requirements on POPs which are currently more stringent than those included in the Stockholm Convention. For example a limit value for PFOS was set, therefore the amount of PFOS used in textiles or other coated materials should be lower than 1 µg/m² of the coated material or that the phase out the PFOS containing fire fighting foams had to be done by 27th of June 2011.

Therefore Romania, through Ministry of Environment and Climate Change, conducted during 2011 to 2012 a NIP updating process at national level. In October 2012 the updated version of the NIP was submitted to the Stockholm Convention Secretariat.

The updated National Implementation Plan provides a description of POPs issues in Romania including the description of implementation activities in the past six years with regard to the 12 legacy POPs. Further it describes the inclusion of the 10 new listed substances in the NIP. The implementation plan also describes Romania's new initiatives with a view to further implementation of the Convention in respect to all listed POPs.

The overall purpose of the updated NIP on Persistent Organic Pollutants (POPs) is to fulfill legal obligations, increase awareness of POPs and their control measures, and also to take of the necessary action

and lay down a strategy and action plans for further measures related to all listed POPs.

For an effective implementation of the measures laid down on updated NIP and achievement of its eight specific objectives, a Governmental Decision for the amendment of Governmental Decision no 1497/2008 is under approval. This Governmental Decision defines the overall objective, the specific objectives, the actions to be taken, as well as the responsible authorities and the timeframe for NIP implementation.

Approach, Achievements and Results

The Ministry of Environment and Climate Change contracted the National Institute for Research and Development in Environmental Protection (INCDPM) to carry out the NIP update.

First step in the updating process was organizing the national coordination meeting to initiate the preparation for the review and updating of the NIP. The objective of the meeting was to raise awareness among stakeholders about the addition of the 9 new POPs to the Stockholm Convention,

to gain the political commitment to the process and to establish the structure and procedures for executing the process.

Among the stakeholder we can mention representatives from the ministries of environment, health, labor, agriculture, industry, transport, regional development, science and technology, academia, research institutes. It is important to mention that many of the governmental and non-governmental bodies that had participated in the development of the initial NIP were also involved in the review and update process.

During the national coordination meeting the stakeholders were consulted with the following areas: import and export (required to control POPs flows into and out of the country and as a possible source of information on articles containing new POPs on the national market); industry (affected by regulations on production/disposal of waste and articles containing new POPs); waste disposal and recycling (affected by regulations on the disposal of new POPs and the recycling and disposal of articles containing new POPs).

The next step in NIP update was to determine the baseline situation with regards to the new POPs listed in the Convention. A preliminary inventory of the presence

of the new POPs within the country was conducted in order to collect data on production, distribution, use, import and export of new POPs, institutional setting and infrastructure for management of new POPs, environmental contamination and exposure and enforcement mechanisms. For carrying out the preliminary inventory the team used the Guidance for Developing a National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants (updated in 2012 to include the POPs listed in 2009 and 2011) provided by the Stockholm Convention Secretariat.

Therefore, a national survey was conducted to fill in data gaps on the presence of new POPs in the country. In this sense, was developed an interactive website page on which were uploaded questionnaires for POPs data collection, as well as for public awareness on issues related to POPs. The logical structure of the questionnaires was translated into an online platform, platform served by open source solution “Limesurvey”. The platform runs on an external server connected to the internet with its own domain and a public IP address.

The preliminary inventory concluded the followings:

- Alpha and Beta – HCH is likely to be found in the Lindane contaminated sites on the and around the former chemical platforms that produced Lindane in the past.

- No waste stockpiles contaminated with or containing Clordecene have been reported.

- Although in the 70s this substance was used as a flame retarder, no information is currently found on the production and use of hexabromobiphenyl, as well as on the existence of waste stockpiles contaminated with or containing this substance.

- No information was found regarding the production of Hexabromobiphenyl ether (hexa-BDE) and Heptabromobiphenyl ether (hepta-BDE), but there are several articles in use, which contain it.

- There is no production of Tetrabromobiphenyl ether (tetra BDE) and Pentabromobiphenyl ether (penta BDE), but there are in use several articles containing it. At the level of 2009, a total quantity of 3000 kg of Pentabromobiphenyl ether containing waste (plastic materials for electronic equipments, textile materials, protective clothing, curtains, lavettes) was generated, out of which 1250 kg were eliminated and 1750 kg are still in stock.

- Regarding the existence of the stock of waste containing lindane, in the year 2009, there was a stock of 563 kg Lindatox identified in Teleorman County, from former agricultural cooperative. According to the data from Teleorman EPA, the total amount was eliminated in 2010.

- At the national level, it is likely that PeCB emissions from many primary sources have also been reduced in recent decades, due to the closing down of most of the industry sectors, but there are still uncertainties concerning the total quantities released.

- There was no production of Endosulfan, but following the request and notification to the Commission by Ministry of Agriculture and Rural Development, in accordance with the provisions of Article 8 of Directive 91/414/EEC, this product was imported and used as raticide. The quantities of pesticides containing Endosulfan used at the level of 2011 were of 41750 liters. There are no Endosulfan stocks left.

- Currently, there is small scale usage of substances containing PFOS, PFOS salts or precursors of PFOS in metal coating processes.

- Concerning the textile materials, there is no use of chemicals containing PFOS,

PFOS salts or PFOS precursors in the production process, as well as there is no production and use of products manufactured by recycling textiles produced before 2003* (*the year of 2003 has been recognized as the threshold year when the use of PFOS has been discontinued in commercial repellent chemicals).

- In the field of production/import of synthetic carpets, there are no chemical substances used for the treatment of carpet surfaces, and there is no use of products made of by recycling synthetic carpets, produced before 2003, having PFOS content, as well as no production or placing on the market of synthetic carpets with PFOS, PFOS salts or PFOS precursors content.

- Neither for the pulp and paper sector, no use of chemicals containing PFOS, PFOS salts or PFOS precursors.

- In case of waste treatment, production of semiconductor, electronic and photographic sector there is no information on the use of chemicals containing PFOS, PFOS salts or PFOS precursors, or on the existence of stocks of waste containing these substances.

- Regarding the use of PFOS in fire fighting foams, this was allowed until 27 June

2011 according to the EU legislation. At the level of Inspectorates for Emergency Situations foams containing PFOS, PFOS salts or PFOS precursors are not used. Concerning the type of foams existent in stock, there is no information available.

- The quantities of PFOS containing waste in Romania at the level of 2009 were of 1000 kg, which were eliminated.

In addition to baseline data on the presence of new POPs, the information was collected on the status of “old POPs”, as well as the legal framework and institutional infrastructure in place to meet the

requirements of the Stockholm Convention with regard to the new POPs. The starting point was the information already present in the initial NIP, which was reviewed in order to identify achievements of the first NIP implementation, as well as the information gaps and deficiencies that should be addressed in light of the listing of the new POPs under the Convention.

The following steps of the NIP review update process resulted in the identification of the priority issues to address in the management of new POPs. A set of 8 key objectives (see Table 1) guiding the development of preliminary country activities

relevant to new POPs was established, taking into account the following criteria:

1) to what extent a particular key objective should be addressed in the national environmental protection strategy;

2) to what extent it is considered the responsibility of the involved authorities involved in the initiation, planning and implementing the actions needed to achieve a particular key objective; and

3) to what extent does a particular key objective address directly the most severe environmental problems caused by POPs substances.

Priority	Key Objective	
I	Key Objective 1:	Elimination of brominated diphenyl ethers from the waste stream
II	Key Objective 2:	Risk reduction for perfluorooctanic sulfonic acid (PFOS) with its salts and perfluorooctanic sulphonyl fluoride (PFOS-F)
III	Key Objective 3:	Elimination of PCBs containing equipments
IV	Key Objective 4:	Reduction of unintentional emissions of POPs
V	Key Objective 5:	Improvement of environmental protection performance in agriculture
VI	Key Objective 6:	Remediation of POPs contaminated soils
VII	Key Objective 7:	Information and public awareness
VIII	Key Objective 8:	Research and development

Table 1: Key-Objectives

Based on the 8 key objectives, the NIP review team identified the possible management options and drafted the corresponding action plan. The action plan included measures for:

- identification of articles containing hexabromodiphenyl ether, heptabromodiphenyl ether, tetrabromodiphenyl ether and pentabromodiphenyl and their presence in the recycling and waste streams;
- coordinating the actions on BDEs with the programmes on the management of electronic waste, with the ultimate aim of elimination of BDEs from the waste stream;
- risk reduction and elimination of PFOS, its salts and PFOS-F, and promoting the use of alternatives to these chemicals;
- reduction or elimination of releases from unintentional production, including the measurement or estimation of releases of pentachlorobenzene from source categories;
- elimination of PBCs containing equipments;
- sustainable use of pesticides in agriculture;

- identification and remediation of POPs contaminated soils;

- increasing public awareness concerning threats imposed by POPs.

The proper national framework for the implementation of the National Implementation Plan will be set by a Governmental Decision, currently under approval, that establishes the following:

- coordinating national authority for the NIP implementation;
 - coordinating national authority for preparing the annual report on status of implementation of NAP;
 - authorities responsible for the implementation of actions needed to achieve the 8 key-objectives identified in the NIP;
 - timeframes for NAP implementation and for reporting on the status of implementation of NAP.
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ACTUAL ECOLOGICAL AND RESOURCE PROBLEMS FOR THE TREATMENT OF PERSISTENT ORGANIC POLLUTANTS

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After the collapse of the Soviet Union, the Ukraine received strong industrial infrastructure with very high potential and anomal technogenic pressure on the main ecological systems: soils (60% of ploughed lands), hydrosphere (70% technogenic deformed), geological environment (more than 2800 mine objects), biosphere (about 1000 of Red Book species).

Besides, the territory of the Ukraine has the accelerated geomigration of POPs in the surface and underground hydrosphere due to active development of the water irrigation systems, regional depressions of groundwater intake systems, mines and pits, high vulnerability of groundwater within the most hydrogeological structures (northern, central and southern regions).

However, many manufacturing processes are not flawless in terms of environmental protection. This applies, in particular, to the use of modern agricultural production of the country with a large number of pesticides. In particular, their unused balances

are a source of income in the agriculture geochemical landscape, biosphere and foodchain of various chemical substances that cause irreparable damage to the environment. Therefore, the daily problem of allocation and utilization of pesticides has become more urgent.

An increase in funding for environmental programs of the Government of disposal of pesticides (the Ukraine has accumulated more than 20 thousand tonnes of pesticides) is associated with two important issues. First is the development of new innovative technologies for the processing of hazardous chemical waste in special bioreactors. This technology involves mixing products chemicals (pesticides) and special microorganisms that break down hazardous substances.

The second and the most important one has to do with increasing environmental security in the Ukraine and demonstration of European thinking on the eve of the signing of the Association Agreement with

the European Union. The European Community approach based on the fact that global environmental threats are the main risks of social and economic system of the state. As a consequence, these become an obstacle to economic prosperity and sustainable development of any country.

In general, considering the nature of European integration of the Ukraine on the eve of the summit in Vilnius, the arrangement of the common EU space not only in economic, social and political spheres, but also in eco-environmental protection. Thus, special attention is paid to the Agreement with the EU mechanisms for solving environmental problems in the context of a secure European space based on innovative clean technology manufacturing and recycling.

Today the EU has the highest rate of achievement in the field of environmental and powerful management mechanisms to strengthen national environmental policies. European states have long had the

status of environmental policy leaders in the world today confirming recent ranking by the World Economic Forum.

Now one of the most pressing environmental problems are savings disposal of hazardous waste. Only the amount of accumulation of obsolete crop protection chemicals (hereinafter - OCPC) at the beginning of 2009 was more than 22 thousand tonnes. The volume of hazardous waste generation in Ukraine in 2009 (the last year in which the forms of state statistical reporting number 1 - hazardous waste) exceeded 1.2 million tonnes, and total savings - 20.8 million tonnes.

Modern fitted storage for storing hazardous waste management and disposal of their established only in individual enterprises that virtually have no effect on the overall situation. The number of specialized companies in this field is extremely insufficient. Lack of appropriate conditions for the utilization and disposal of hazardous waste leads to their accumulation in industrial areas.

The problem also lies in the lack of science-based concepts of processing and disposal of hazardous waste, poor implementation of proven best modern technology, imperfections in manufacturing processes and technology cycles

incompleteness processing raw materials, low-effective system of collection, lack of safe methods of disposal or location, etc. by the World Economic Forum.

In recent years, due to the reform of the agricultural sector has repeatedly changed owners unsuitable OCPC. This resulted in a large number of abandoned OCPC loss documentation destruction warehouses, containers and packaging materials, and, consequently, to the formation of a large number of unknown and mixed.

Determining of the actual amount of useless OCPC not allow a significant number of abandoned (natural) sites of accumulation, inadequate visual assessment of their weight without direct weighing due to the presence of high risk during inventory.

According to some available reports of MAP, only in 1967 and 1968, drugs from the group of POPs in the Ukraine were applied to the total number of 8470.6 tonnes. The 1971-1990 period was characterized by consistent implementation in practice declared in the sixties prohibitions and restrictions on persistent organochlorine pesticides. The prohibition of the use of these pesticides has led to the accumulation of residues in warehouses and in households so-called "raysilhosphimiyyi" Ukraine- state regional for centralized and

planned distribution of the POPs without taking into consideration of the assimilative potential of agriculture landscapes and biosphere including the local population.

By 1995, the Ukraine has been a manufacturer and exporter of only one pesticide, referred to the group of POPs, such as DDT. Since 1986 its production was discontinued in the Ukraine.

As the technology to recycle the majority of hazardous wastes that meet environmental regulations and standards in Ukraine is not implemented, there is no appropriate infrastructure, removal of hazardous waste from the Ukraine performed as a necessary measure for their safe disposal at specialized enterprises of other countries. Experience removal of obsolete pesticides in recent years shows that the true figure may at times exceed predefined volumes.

In 2010, the Ukraine started the implementation of practical measures aimed at eliminating the most significant accumulations of hazardous waste, including mixtures "Premix" smuggled in the region; removal of obsolete pesticides; hexachlorobenzene waste landfill of toxic industrial waste in Kalush district, Ivano-Frankivsk region; mononitrochlorobenzene waste from the territory of State "Gorlivka chemical

plant”; wastes containing beryllium from the territory of SSPE “West” (m. Kyiv).

Financing activities aimed at solving the problems accumulated over previous years hazardous waste carried from the Reserve Fund of the State Budget of the Ukraine, State and local funds for environmental protection. During 2010-2012, these goals were directed more than 1.5 billion. However, the existing distribution of environmental tax, in which 90% of the money goes to local budgets, obviously, the ratio of funding measures need revision upward expenditure of local funds for environmental protection and broader fundraising owners waste.

The Cabinet of Ministries has increased funding for the implementation of the National Action Plan for Environmental Protection of Ukraine for 2011-2015. Thus, an additional 280 million UAH will be allocated and directed to the disposal of waste pesticides and agrochemicals. In addition, funds will be allocated to utilize more than 8 thousand tons of waste hexachlorobenzene, located in zone of the unsaturated filtration above of groundwater aquifer in the area of conservation Dombrowski career in Ivano-Frankivsk region.

Increasing environmental challenges significantly affect the economic system

of the state. It manifests itself not only through environmental damage, but also because of the financial losses of the national economy of the Ukraine. Thus, an effective system of disposal of chemical waste needs to be developed today. Processing of chemical waste industrial and agricultural sectors of the Ukraine in line with European environmental standards are important and paramount tasks of the national environmental policy.

Action Plan № 589 to implement the Stockholm Convention on POPs approved by the Cabinet of Ministers on 25th July 2012 provides the following:

- Strengthening the institutional system.
- Removal of accumulated unusable and prohibited use of chemical plant protection products, industrial waste of persistent organic pollutants.
- Removal / disposal of waste and equipment containing polychlorinated biphenyls.
- Elimination or reduction of emissions of persistent organic pollutants (in accordance with Annex C of the Stockholm Convention) due to unintentional production.

- Identification of the areas contaminated with persistent organic pollutants.
- Exchange of information on POPs with stakeholders and raising awareness.
- Creation of a system for monitoring persistent organic pollutants.
- Conducting research.

The principles of national policy on the treatment of POPs:

- Identification of contaminated sites, to determine the level of danger and urgency of response;
- protection of people and the environment from the harmful effects of POPs due to reduced leakage and emissions of POPs, stop using POPs and equipment containing POPs;
- promoting cooperation between interested parties who are directly or indirectly involved in issues related to POPs, or are able to solve them;
- adequate solution to the problem of emergency and banned for pesticide use, emissions and industrial waste from the group of POPs;

- effective management of toxic chemicals throughout the life cycle in order to avoid, prevent or minimize emissions and their negative impact on human health and the ecological parameters of environment;
- Attracting investment to implement measures to reduce or eliminate the threat of negative impact of POPs on human health and the environment.

The directions of state policy in the sphere of POPs are as follows:

- improvement of relevant legislation;
- organization of monitoring places of accumulation of POPs, including by means of bioassay;
- Selecting the best technology solutions for environmentally safe disposal or destruction of POPs in their places of storage;
- inventory of measures to identify and evaluate new number 9 POPs added to the list of the UN Fourth Conference of the Parties of the Stockholm Convention in May 2009;
- identification and implementation of organizational environmentally friendly

technological solutions to reduce the risk of contamination, disposal or destruction of POPs;

- ensure the safe storage of chemicals classified as POPs group, revealed in their custody;
- rehabilitation of contaminated territories POPs;
- implementation of measures to prevent further accumulation of POPs in warehouses farms.

The priorities in the management of POPs include the following:

- development of national legislation that should govern the treatment of POPs in accordance with the requirements of the Stockholm Convention;
- improved monitoring of POPs in the Ukraine in the according with protective ability of soils (agriculture landscapes),- surface and underground hydrosphere and biosphere within different regions. ;
- legislative support for keeping and maintaining the State Register of storage and the number of agents assigned to the group of POPs; inventory of emergency stocks by international standards and imple-

menting accounting system for pesticides PSMS;

- selecting the most appropriate environmentally sound technologies of economic destruction (neutralization) POPs according to security requirements based on international standards;
- disposal of banned and obsolete pesticides for use referred to a group of POPs and waste disposal equipment containing PCBs, using suitable modern environmentally friendly technologies;
- elimination or reduction of emissions of POPs;
- development of an analytical framework for improved monitoring of POPs;
- identification and rehabilitation of land and areas contaminated with POPs, using modern, including agro-biotechnology;
- an active information policy to the public and interested parties on POPs;
- mobilizing resources and providing financing, including attracting foreign investment to implement the National Plan implementation of the Stockholm Convention on POPs in the Ukraine;

The basic directions and tools for solving

the problem of hazardous waste disposal savings, including the establishment of appropriate national infrastructure, should be implemented within the framework of the National Programme of waste in the period of 2013-2020, which project through the approval procedure in the relevant central executive bodies.

In modern terms, the problem of accumulation of waste production and consumption is one of the leading threats to environmental security. There is a growth of waste, including hazardous chemical, significantly extend the area of illegal dumps. In addition, the process of pollution of river network waste coal, chemical and metallurgical industry, municipal infrastructure and agriculture. This extremely inadequate introduced modern technology to attract commercial waste treatment, hardly used positive international experience in waste management and regulation of hazardous substances.

In connection with the completion of the period of implementation of the National Program of toxic waste (adopted 14.09.2000) and Applications of waste production and consumption by 2005 (adopted 06/28/1998) today the state does not have a policy document in the field of waste management.

In the absence of appropriate conditions, the removal and disposal of hazardous wastes is their accumulation in industrial areas. Today the Ukraine has not implemented any technologies to recycle the majority of hazardous waste in accordance with international standards in the absence of necessary infrastructure. The National Programme of waste for 2013-2020 has not been approved yet.

Some actions on solving the problem of household waste disposal are being taken at 6000 polygons covering about 9000 hectares and partially recycled at waste incineration plants. The service of household waste provided only 75 percent of the population each year, leading to the formation of new illegal dumps. Most landfills are overloaded or do not meet the requirements of environmental safety. Additional dangerous are connected with the disposal of waste sites in the ravine' valleys, abandoned local pits, etc., where groundwater surface is situated too close to surface.

Despite the orders of the President of the Ukraine from 30.05.2011, to date, there is no effective management system with worn tires, and waste products from industrial rubber production, waste oil, elements of electrical and electronic equipment.

Due to the lack of separate collection of

solid waste and poor economic incentives, promoting the use of waste as secondary raw materials in the state lost significant financial resources with increasing negative impact of waste on the environment. In addition, the lack of proper coordination of executive power is not fully meeting the requirements of legislation on waste as secondary raw materials.

The situation raises serious concerns with the handling of medical waste and waste medicinal products does not protect people and the environment from its harmful spatially developed and complex effects. The state of legal regulation in this area is ensuring the creation of an effective system of collection, removal and disposal of waste healthcare system and substandard medicines.

The situation that has developed in the field of waste management poses a real threat to public health and the environment in the? Ukraine. Given a large-scale nature of the problem of efficient waste management in the country, it seems appropriate to take a number of measures at the legislative and executive level to address these issues.

At the level of the Cabinet of Ministers of the Ukraine:

1. Submit a draft law on national program of waste management in the Ukraine to the Parliament of Ukraine.

2. Ensure the development and operation of information and analytical support system of state administration in the field of radioactive waste in order to provide adequate information on the state waste management system.

3. Organize the preparation and approval of complex legal, and technical measures aimed at creating infrastructure with gathering, storage and disposal of used tires, and waste products of industrial rubber production; collection, removal, disposal and recycling of waste oils; collection and recycling of waste electrical and electronic elements equipment; treatment of medical waste.

4. Ensure that the established procedure addressing the issues of determining the issuance of permits for operations in the waste management procedures and improve the development, approval and revision of limits on waste generation and disposal.

5. Develop a draft law on waste management as a secondary resource issues including recycling of waste, waste packing material and man-made mineral deposits.

6. Establish a mechanism for financial and economic preferences in the field of waste management, which involves waste into circulation as additional sources of energy and raw materials.

7. Harmonize existing national legislation in the field of waste management with European directives in this area including the new version of the classifier of waste.

HBCD PHASE-OUT IN THE STOCKHOLM CONVENTION

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The Stockholm Convention Conference of the Parties decided to add a new brominated flame retardant, hexabromocyclododecane (HBCD), in the Annex A of the Convention in May, 2013. HBCD is mainly used as a flame retardant additive in polystyrene insulation products (EPS and XPS), but also, to some extent, in textiles and high impact polystyrene (HIPS) plastic. HBCD is the third brominated flame retardant considered a persistent organic pollutant (POP) by 179 countries and, subsequently, included in the prohibition Annex A of the Stockholm Convention.

HBCD was introduced to the market in the 1960's and has been used to produce self-extinguishing polystyrene insulation materials since the 1980's. It is understood that the wider use of the flame retarded polystyrene insulation started in the 1980's. The concentrations in polystyrene insulation vary between 0,5 % in expanded polystyrene (EPS) to 4% in extruded polystyrene (XPS), depending on the fire

safety requirements. The use in high-impact polystyrene (HIPS) for electric and electronic products has been minor, and, according to the present understanding, HBCD has been replaced by cheaper alternatives. In textiles, HBCD is used in backcoatings for upholstery and other interior textiles, including automotive applications. The use of HBCD for that has decreased due to its price and cheaper alternatives. There are, however, still certain uses where HBCD has been considered preferred.

HBCD is produced in the USA, the Netherlands, Israel, and China. The use volumes prior to the Stockholm Convention listing were approximately 30 000 tonnes per year, globally. Compared to the previously prohibited commercial brominated flame retardants c-pentaBDE (listed through its tetra- and pentabromodiphenylether congeners) and c-octaBDE (listed through its hexa- and heptabromodiphenylether congeners), the cumulative amount

of HBCD used is manifold and has been increasing for the last decade. The main share of the market volume is used in Europe and China (approximately 40% each), and the rest in Japan, Americas, and Korea. The products and articles containing HBCD are exported to other countries too.

HBCD was considered to likely cause significant adverse effects on humans and/or environment, because of it being persistent, bioaccumulative, very toxic and undergoing long-range transport. HBCD is found in blood, plasma and adipose tissue in humans. The main sources of exposure presently known are contaminated food and dust.

The Stockholm Convention decision clearly flags the substance for phase-out. However, the decision allows the parties to continue using HBCD for producing certain EPS and XPS for 5-10 years because the alternative flame retardants were not

fully available commercially at the time of listing. It is necessary to highlight that the specific exemption granted allows the production of HBCD containing polystyrene insulation materials only for buildings, but not for packaging, ground frost insulation or civil engineering applications. Thus, despite the transition period, some major uses of EPS and XPS as well as the use in textiles and HIPS will need to be phased out immediately upon ratification.

Several alternatives to replace HBCD have been commercialized, and it is expected that at least one alternative will already be available in sufficient quantities in Europe, Japan and North America in 2014. In addition, there are alternative insulation materials (such as mineral wools) and construction techniques are available to replace EPS/XPS in many uses. In HIPS and textile, the list of alternatives is long. Despite the availability of the alternatives, the specific exemption meets the industry needs for additional time to adjust their production processes and certify the new products.

The available assessments estimate the environmental emissions of HBCD during the production and use to be small, compared to the release from products during

their use and end of life waste. HBCD emissions to indoor air from products made from EPS or XPS during service life when installed are estimated to be low, although the estimates concerning releases during consumer use of HBCD containing articles are highly uncertain. It is clear, however, that HBCD is present in house dust.

Emissions from HBCD-containing materials will be a potential long-term source to the environment unless properly managed. Most of the produced volume of HBCD ends up in articles, mainly in polystyrene (XPS, EPS) used in the construction and building sector, but also in packaging. The likely future emissions from such articles have not been assessed. The life span of polystyrene foam in buildings is reported to be 30-50 years. The use of HBCD in insulation boards and the HBCD built into buildings and constructions is increasing, and it is likely that the release from EPS/XPS will be more significant in the future; particularly, from about 2025 onwards, as increasing number of buildings containing HBCD retarded EPS and XPS will be refurbished or demolished. This turn-over will be different in different regions, and range from 10 to 50 years.

HBCD historical and current use varies largely from country to country, thus, having a major impact on a country's obligations to deal with HBCD containing materials as POPs waste at the end of their service life. Consequently, different countries will have very different problems in managing HBCD-containing waste when buildings are demolished or renovated. For some countries, the problem will be small, and for others, in practice all polystyrene can be considered POPs waste. The listing may also have a significant impact on polystyrene recycling, as recycling of HBCD containing products will be banned upon listing. The waste problem is accumulating, and the amount of HBCD-containing waste increasing in many developed countries, since insulation materials are used for 30-50 years. Textiles, HIPS and packaging material will enter the waste management a lot sooner.

Packaging waste is a specific challenge: it is widely transported and currently also recycled and should in principle be HBCD free. However, even packaging EPS is sometimes flame retarded because of logistical reasons: the EPS raw material available on the market is predominantly made for insulation use, and, thus, the raw material used for packaging may be flame

retarded just because such beads are available on the market and non-flame retarded material would be a specialty. The packaging material life-cycle is, however, relatively short and as soon as HBCD will be phased out, the packaging material stream will be cleaning from HBCD fast.

Added challenge in ensuring waste management according to the Convention is that it is not easy to distinguish HBCD-containing materials from those which are HBCD-free. In practice, the identification of POPs waste containing HBCD must be based on the knowledge of national fire safety standards, year of construction, building codes and other regulations and practices of the time, and source of polystyrene products used in the country. A new element in the Convention listing is that the companies producing HBCD-containing EPS/XPS insulation for buildings under the exemption, will need to label or otherwise make the HBCD products identifiable. This will, however, not improve the situation for HBCD containing material already on the market.

CRITICAL EVALUATION OF THE EFFECTIVENESS EVALUTION OF THE STOCKHOLM CONVENTION MEASURES

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We have a lot of problems with the state of our planet's environment, we have problems with chemicals on the planet with their often highly complex mixtures. These problems pose a risk to the long-term environment and human health. Addressing these issues requires a broad and highly effective international cooperation. Despite tremendous efforts, a number of activities and projects well done, the key question is whether the effectiveness of activity of the international community in the UN would not be significantly higher. It is extremely important to have perspectives from the current economic crisis, critically evaluate the relationship between funds spent and the results obtained. It is necessary to critically evaluate the relationship between the resources embedded in the organization of conferences, expert meetings, workshops, tours (sitting time) and resolution procedure in individual countries (resolution time). How to carry the participation of representatives of each country largely funded from international

resources to solve problems in these countries. It is necessary to critically assess whether it would be possible these (sitting) resources better invested in solving problems, solving specific problems in individual countries.

GLOBAL POPs MONITORING AND CURRENT STATE IN THE CEE COUNTRIES

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Article 16 of the Stockholm Convention on Persistent organic pollutants provides the basis for the effectiveness evaluation of the Convention and the Global Monitoring Plan. Monitoring data on POPs are a major component of the effectiveness evaluation process, in addition to data from national reports submitted pursuant to Article 15 and reports on non-compliance once the procedure is adopted by the COP, as well as reports and other information provided pursuant to paragraph 2 of Article 16.

In addition to implementation aspects, the second phase of the GMP includes work on updating of the guidance document to fully address the 10 newly listed POPs and the harmonized structure for GMP data handling, evaluation and presentation. An expert group meeting was held in Brno, Czech Republic in June 2012, helping to better identify the attributes that such a GMP data handling tool needs to have. The work on the GMP data handling also

aims to address the appropriateness of the GMP data for the effectiveness evaluation; similarly, the revision of the reporting format to address the suitability of the reported data for the effectiveness evaluation will also facilitate the process of evaluating the effectiveness of the Convention.

The updated guidance document¹ on the global monitoring plan for POPs properly addresses the sampling and analysis of the newly listed POPs, and provides a useful basis for monitoring of these chemicals in the second phase of the global monitoring plan, and for harmonized data collection, storage and handling. The coordination group encourages the use of the updated guidance document by the regions and communication of feedback on using the guidance via the regional organization groups. The current situation in the Central and Eastern European region will be discussed.

¹ UNEP/POPS/COP.6/INF/31.

POLYGON OF TOXIC WASTE OF HEXACHLOROBENZENE NEAR KALUSH TOWN IN UKRAINE REMAINS A THREAT TO WESTERN UKRAINE AND TRANSBOUNDARY WATER BODIES

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Introduction

Kalush is a major center of chemical industry in western Ukraine, the administrative part of the Ivano-Frankivsk region. The industry was focused on Kalush chemical and metallurgical complex (KChMC), founded in 1968, near the large Kalush -Golinskaya potassium salts deposit. Potassium salts were mined by open - pit (Dombrivskii quarry) and mining methods. Dombrivskii quarry is the world's only mountain, to where salt extraction was carried out openly. During the operation period of Dombrivskii career (1967 -2000), the operated volume was 52.5 million m³. From the northern part of the quarry, 14.6 million tons of ore (depth production was 63 m) were extracted; the southern part of the quarry produced 17.3 million tons of ore and 20 million tons of recovered rock (depth of production - 127 m). At this time, the career is flooded by atmospheric and ground water to the point of 274 m. The upper layer of water in this

career is salty; more than 16 million m³ of brine have been accumulated in the lower layer. External dumps and the pit itself are destroyed by salt karst.

KChMC consisted of 12 plants specializing in the production of potassium fertilizers, magnesium fertilizers and its compounds, products of hydrocarbons chlorination. Subsequently, the production was expanded and reorganized into the chemical company "Vinil chloride", later - in concern "Oriana-Galev", which lasted until October 2001 when the factory was closed.

The production of perchlorethylene and carbon tetrachloride was carried out by concern "Oriana-Galev" industrial chlorination of hydrocarbons, mainly methane. The main component of waste generated as a by-product of this process was hexachlorobenzene (HCB), the content of which in waste was 53 - 67% [1]. This substance has strong toxic properties in accordance with the list of the Stockholm

Convention on "persistent organic pollutants" (POPs), refers to the class of substances banned for production and use [2].

As a result of long and ill-conceived mining activities, mining of potash ores in Kalush-Golynska field and their processing on these chemical plants near the town of Kalush and villages Kropivnik and Sivka Kalushska, environmental emergency has been developed. These areas are potentially dangerous for the life of the people because of the many failures of the earth surface, the destruction of homes and communications, salinization of drinking water sources. In the area of intensive subsidence of the earth's surface above the mine workings located about 1.3 thousand of residential units and 23 industrial plants (Figure 1). The most dangerous objects, according to experts, is spent Dombrivskii career, tailings # 1 and # 2, salt dumps on the sides of the career, sludge depository, potash mines "Kalush", "Holyn", "Khotyn", "Novo-Holyn", as well as ground

solid polygon of toxic HCB waste in Kalush (the Polygon).

HCB Polygon (Figure 1), was artificially created as a result of direct production activities of concern “Oriana-Galev.” Given the lack of Ukrainian technologies and manufactures of HCB recycling, it was decided that the disposal of HCB would be in the Polygon, which is 6 kilometers south-west of the town Kalush [3,4]. This Polygon is environmentally dangerous object - the only European storage of HCB toxic waste.

Operation of the Polygon as a disposal place for toxic substances was carried out from 1973 to 2001. Currently, however, there is some evidence to suggest that the dumping of HCB waste were done at other unequipped and unauthorized places near Kalush [5].

Toxic waste containing HCB were loaded into iron 200 liter drums and were disposed at the polygon, at specific sites excavated to a depth of 4 meters trenches, which were covered with plastic wrap and covered with earth. According to the Polygon passport [3], as for October 2001, when it was decommissioned, there were 11352,5 tones of waste, 11087,6 tons of which - technological waste (gummed) that contain HCB (hazard class 1); 264.9

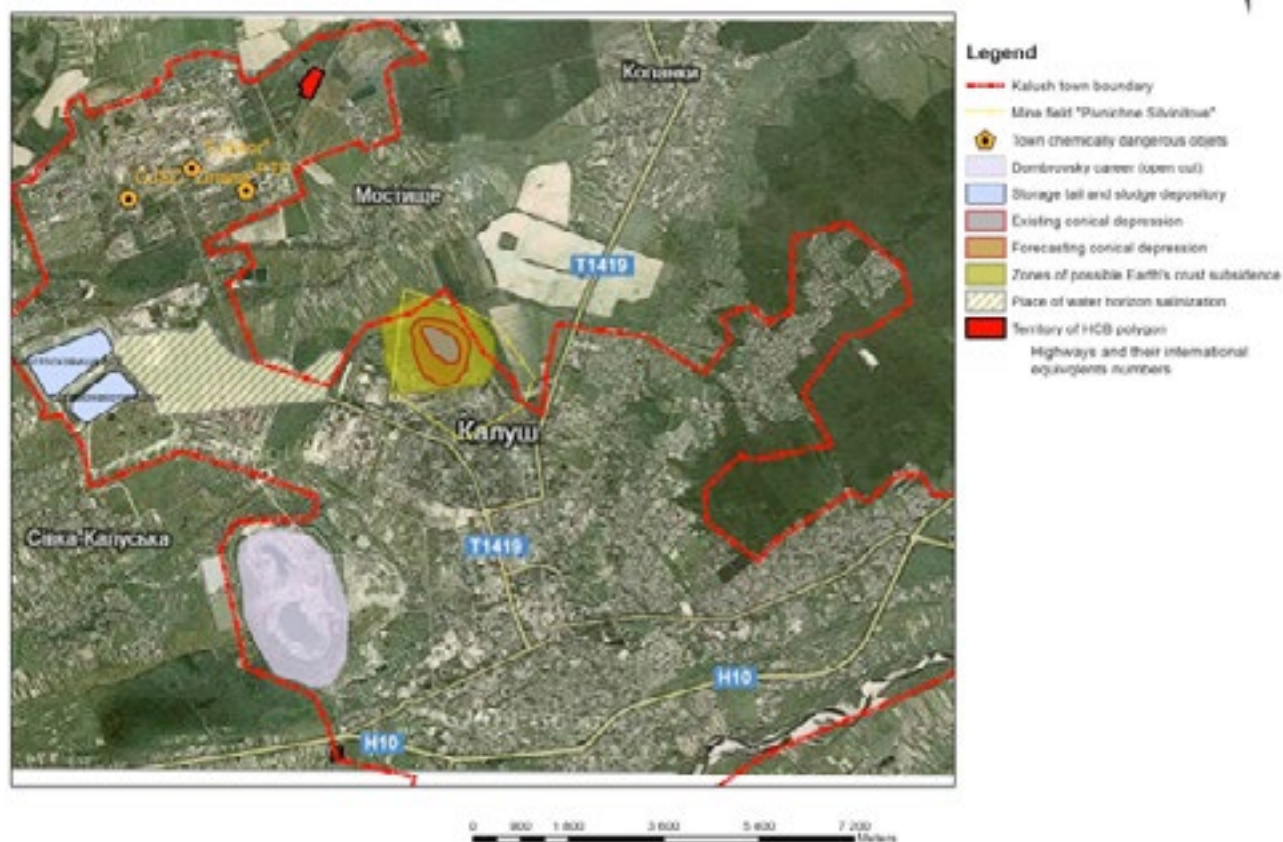


Figure 1: Areas with high environmental hazards within Kalush industrialized and urban agglomeration

tons of solid residues from the equipment (hazard class 3). Highly resinous wood - yellow crystalline substance in the form

of sand with a particle size of 1-3 mm; composition: C2Cl4 – 2-3%, C2Cl6 – 7 - 11%, C4Cl6 – 20 - 27% , C6Cl6 – 53 - 67% [1].

Because of mistakenly selected storage technology, which did not take into ac

count a high degree of flooding of the Polygon site and the aggressiveness of natural waters to metal, these barrels were quickly corroded and damaged. As a result of these processes, HCB as well as other

toxic components got freely in the soil and groundwater and began to migrate, contaminating them. After the 2008 monitoring data have been documented cases of pollution of air, soil and groundwater in the area of polygon and near it, including in the creek of Sapogi - Limnytsia Rivers basin, a tributary of the Dniester. These data suggest that there was violation of the integrity of packaging of waste and HCB started uncontrollably enter the environment.

Taking into account dangerous situation in the area of Kalush town, by the Presidential Decree and relevant decree of the Cabinet of Ministers of Ukraine in 2010, it was decided to dispose toxic waste and to eliminate the Polygon [6, 7].

According to this decision, in 2010 - 2013, in accordance with Article 6 of the Stockholm Convention on POPs (Ukraine ratified 17.05.2004), the works on the identification and removal of HCB waste and contaminated soil to England and France for their destruction by incineration, were conducted.

Before the work started at the initiative of the Ivano-Frankivsk Regional Administration several inspections of the inventory were conducted to assess the quantity and quality of waste mixtures. However, due

Date	Method	Quantity of HCB waste mixed with soils, tonnes	Notes
30.10.2001	Passport site data	11087,6	Based on the fact of waste packaging loading [2]
20.12.2010	Allocation of space burial barrels HCB using a metal detector; conversion of waste drums download area and assessing the degree of violation of tightness on the results of experimental dissection	22000,50	[7]
23.05.2011	First variant of assessment*	54236,92	soil and clay mixture with HCB [8]
	Second variant of assessment **.	23604,29	soil and clay mixture with HCB [8]
* calculation was made based on the contours of the charts in the HCB Polygon defined instrumentally by SE "Carpathian enterprise of geodesy, cartography and cadastre" taking into account the fact that: the barrels were buried in two rows in height, the diameter of 0.6 m, height - 0.9 m, with volume - 200l, 1 m ³ of mix waste with pebbles and debris according to standard weighs 1750 kg, adopted the thickness of contaminated soil layer with destroyed 2.5m barrels			
** assessment was in real determining the amount of waste per 1 m ² on the results of extraction HCB waste in 2010 with 4472, 63 m ² , which averaged 1945 kg per 1 m ² of waste storage			

Table 1: Preliminary assessment of stocks of toxic waste at the site of hexachlorobenzene near Kalush

to the fact that the waste at the time of examination was already partially migrated, the results of these tests differed significantly (Table 1).

The qualitative composition of the mixture of waste that formed in the polygon area

was investigated in December 2011 by Central Toxicology Laboratory on water

transport (Odessa) [9]. Results of these studies showed that the amount of HCB waste mixture can reach 90%. The remainder of the waste also presents hazardous organic materials, namely:

- in the vapor phase in the samples of soil were: 1,1-dichloroethene; 1,1-dichloroethane; chloroform; carbon tetrachloride; trichlorethylene; 1,2,3-trichloroethane; tetrachlorethylene; 1-bromo-1,2,2-trichlorethylene; hexachloroethane; 1,3-butadiene-1,1,2,3,4,4-hexachloro;
- in water samples after extraction were identified: HCB; chloroform; 1,2-dichloroethane; carbon tetrachloride; tetrachlorethylene; hexachloroethane; 1,3-butadiene-1,1,2,3,4,4-hexachloro.

Toxicological characteristic of polygon HCB waste. According to the Stockholm Convention on POPs, HCB listed in Annex “A” refers directly to the group of the most dangerous POPs [2]. HCB prevailing in these wastes, has a high level of toxicity, is resistant to degradation, characterized by the ability to bioaccumulate, transported by air and water, and actively migrates with some kinds of aquatic organisms. HCB can be deposited at a large distance from the source of release, where they accumulate in terrestrial and aquatic ecosystems. Thus, the long-term effects of HCB and accompanying organic pollutants on humans and the biosphere objects due to extremely high environmental risks that require emergency measures to prevent its harmful effects [10,11].

Studies in the HCB Polygon in 2012 -2013 years. The authors of this publication in the period from 2012 to 2013, were invited to provide scientific support for the removal of waste from the polygon. They also conducted a study on the features of the formation of pollutants in the polygon area, the identification of new areas of unauthorized (natural) landfills, the assessment of pollution migration HCB in

the environment for which information is given below.

The data on the geological conditions of HCB waste disposal within a polygon is represented in Table 2.

Groundwater levels within the polygon lie at a depth of 1.5-2.0 m




Geological section	Depth, M - m	Type of soil	Filtration coefficient, m/24hours
EGE*-1	0-1,9	vegetable layer	-
EGE -2	1,9-2,8	loam	$1,4 \cdot 10^{-3}$
EGE -3	2,8-6,0	clayey silt and peat filtering	1,1
EGE -4	6,0-7,8	loam	$2,6 \cdot 10^{-2}$
EGE -5	7,8-9,3	loam filter	1,1
EGE -6	9,3-11,0	clay	$6 \cdot 10^{-3}$
EGE -7	11,0-25,0	gravel-pebble deposits	8,9

* EGE – engineer – geological element

Table 2: Geological section of Quaternary deposits in the area of hexachlorobenzene polygon in Kalush

To determine the structural heterogeneity of soils, as well as to obtain the information about the levels of groundwater, in early October 2012, geophysical studies by resonant acoustic profiling (RAP) in a complex with a metal detector survey of the territory were conducted at the site, followed by geodetic coordinates referenced designated zones heterogeneity. RAP method recently entered the domestic practice of geophysics and has worked well for solving some practical problems - search and exploration geophysics, hydrogeology; engineering geology, geoscience, glaciology, mining [12 - 15].

According to the results, a refined scheme of Polygon outline maps / HCB waste storage sites was made, which is shown in Figure 2. Based on this scheme, infrastructure landfills of HCB consist of 4 sections and 10 cards. According to the archival

-  - test pit;
-  - indicator hole;
-  - pit-hole.

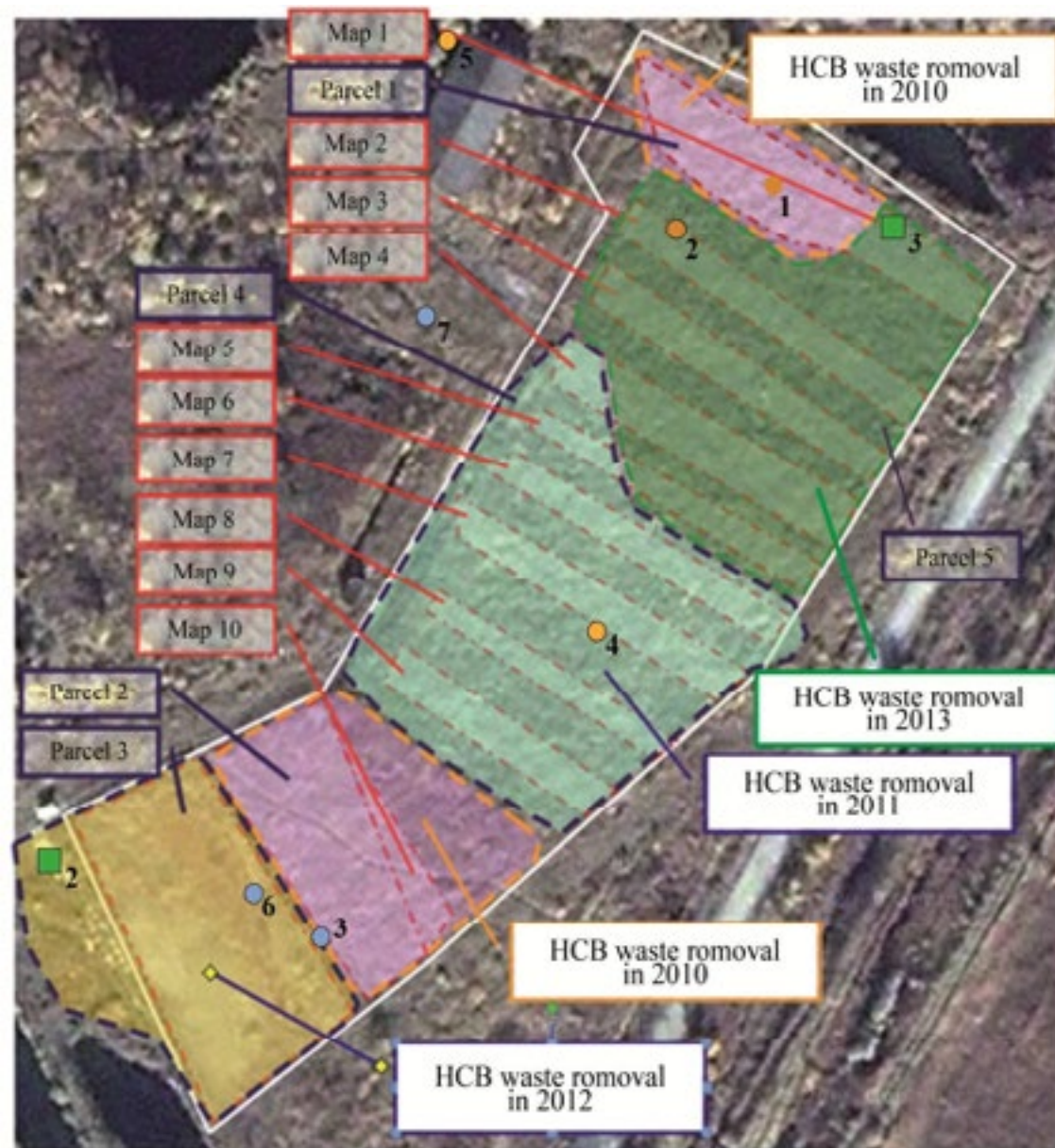


Figure 2: Scheme of HCB waste disposal site with data about the steps of their removal

documents, the bottom card was filled with clay about 0.3 m, which was covered with a polyethylene film (2 mm). The film loaded 200-liter barrels in 2-3 rows (one

another), which overlap the top layer of plastic wrap and bulk clay to 0.5 m.

However, as was established in the showdown, effective protective measures to ensure the safety of barrels of HCB waste from demolition, were absent. Virtually all

packaging waste was in a watered condition that contributed to the development of processes active corrosion and erosion of barrels rust. Documentary photographs (Fig. 3 a, b, c, d), clearly demonstrate the extent of destruction of container corrosion processes (greater than 50% and more). The depth of the groundwater level within the polygon was estimated as 0.15 - 1.7 m.

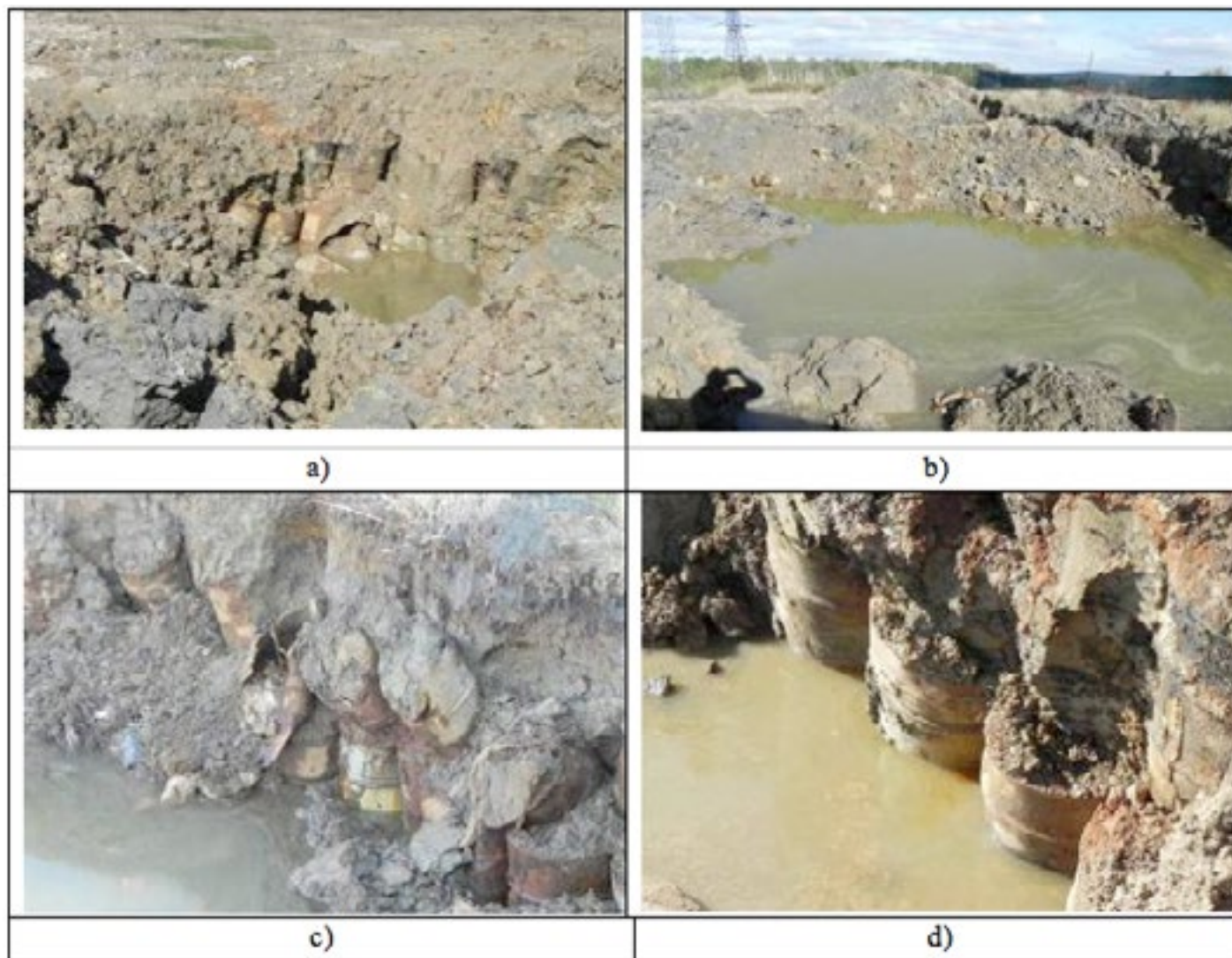


Figure 3: Documentary photographs proving unfavorable conditions for the disposal of packaging waste in the polygon of hexachlorobenzene and activity processes of its destruction

As shown in Figure 2, the infrastructure scheme of Polygon, became the working document for the gradual removal of waste from its territory in 2012-2013. This scheme contains the information about the phases of HCB waste removal from landfills, namely in 2010, was removed 8,514 tonnes of HCB waste mixture; in 2011 - 9,500 tons; in 2012 - 3,430 tons [16]; in 2013 - 8,001 tons. [17] During the period of 2010 - 2013, 29, 445 tons of HCB were removed from the Polygon. Removal and disposal of waste materials from the HCB polygon was to eliminate concentrated focus of toxicological hazard in the zone of Kalush HCB polygon. However, control geochemical soil sampling that was conducted after the removal of the bulk of HCB waste from landfills (as for 20.12.2013) showed very high levels of secondary contamination of HCB in the surface soil layer (Figure 4).

The analysis of the results for determination of HCB in the control soils samples sampled in the surface part leads to the conclusion that after the removal of waste from the polygon and it was filled with clean soil the polygon continues to be contaminated with HCB at around 0.5%

(5 g / kg). This means that the HCB residues in soil at the polygon in 170 thousand

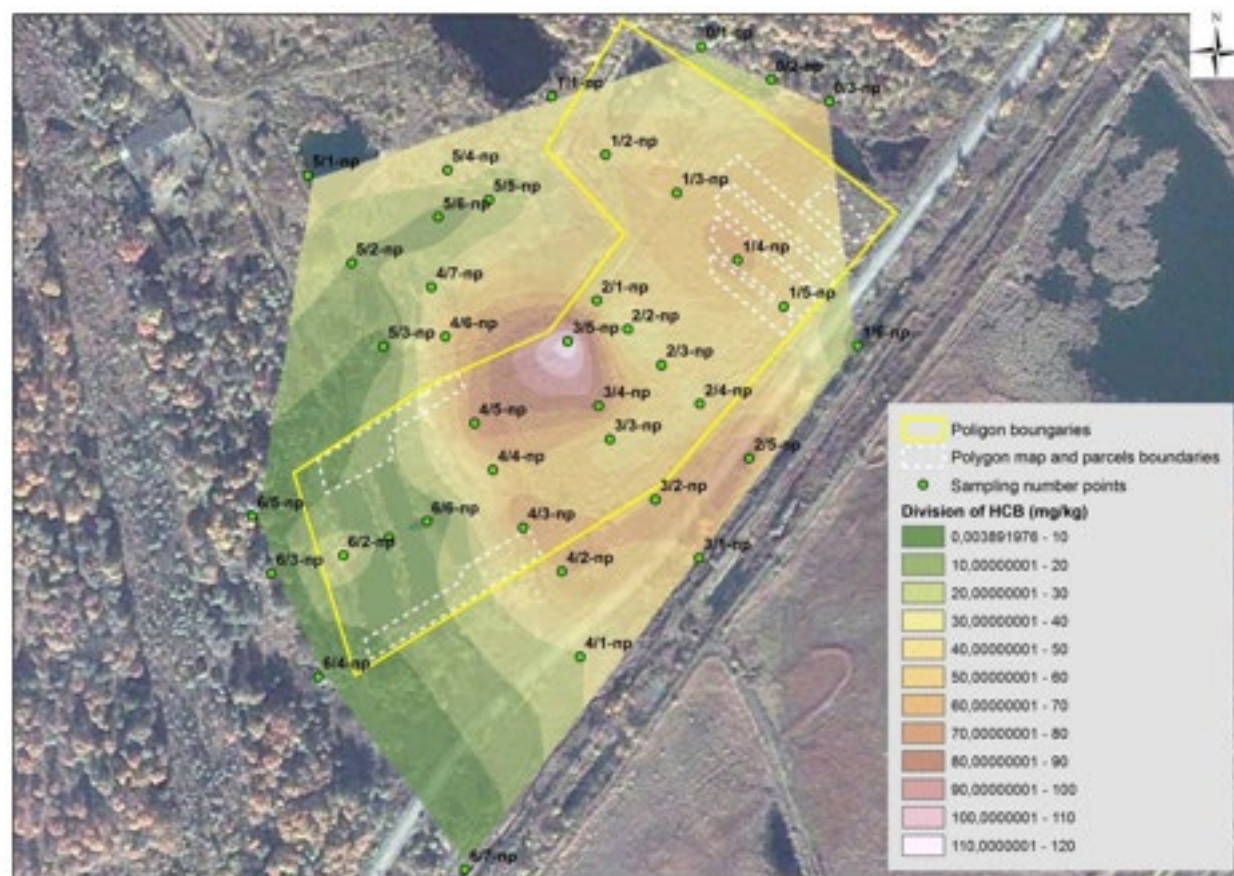


Figure 4: Scheme of the soil secondary contamination levels by hexachlorobenzene at the Polygon, after the toxic wastes were removed from its territory

times higher in comparison with LAC for dry soil.

The presence of significant concentrations of HCB was also recorded in the overburden, which, according [18] to the proce-

dures of removing, were subjected to be stored, and after their removal, these rocks were loaded into a neutralized card. Mass fraction of HCB in overburden is 1.9% (19 g / kg), which is in 6330 thousand times higher than the LAC for dry soil.

This situation clearly indicates that the development of the Feasibility Study for the project HCB waste disposal [18] did not take into account the results of its long-term migration of damaged metal barrels in the upper soil layers. This migration took place in the horizontal direction by mechanical transfer of seasonal changes in groundwater levels and in the vertical direction (upward vertical migration) due to capillary phenomena and evaporation from the soil surface. Partial contamination of overburden could also occur when reopening card operations and waste disposal, particularly when loading peeled waste inundated card overburden at reclamation.

In contrast to the horizontal migration of the sparingly soluble HCB related to its mechanical transfer by filtration through groundwater well permeable sediments, which can be traced on a small scale outside the polygon and the sanitary protection zone, vertical migration caused significant pollution of soil HCB just cut directly in the Polygon.

Conclusions

1. From 2010 to 2013, 29,445 thousand tons of toxic HCB waste was removed from the polygon.

2. Taking into account the assessment of the Polygon safety, after the waste removal, the Polygon remains ecologically dangerous object. The following steps should be undertaken:

- detailed examination to confirm the complete extraction of toxic waste containing HCB, as well as identifying new sources of HCB, which were not neutralized in the period from 2010 to 2013;
- determination of the exact boundaries of HCB contamination spreading outside the polygon;
- designing and implementation of complex rehabilitation measures aimed at localization of residual contamination of HCB within the polygon;
- Monitoring the state of the environmental situation in the polygon and its surroundings.

3. There is a need for a detailed survey to clarify the question of the presence (absence) at the Polygon not previously detected hot spots of HCB. It is based on the fact that during the work on the extraction of toxic waste, in 2010-2013, many aspects of waste disposal technology violations were recorded at the polygon. In the process of waste extraction, were obtained unconditional proof of uncontrolled disposal of waste, containing HCB. Therefore, applied for the period

from 2010 to 2013, technology for waste extraction [18], which was based on the passport of the Polygon and archival documents, could not take into account all the procedures for action cases of violation of the rules of HCB waste disposal. Thus, precise performance of the works that were done by Contractor on the technological requirements of HCB waste removal (TP.04.2011-HCB), does not give an absolute guarantee that at the Polygon is not remained illegally impounded HCB waste.

4. Taking into account the fact that at the Polygon of HCB waste, after their removal and disposal, emerge an extraordinary situation caused by the secondary pollution of soil. So now it will be a great task to ask Food and Agriculture Organization (FAO) to involve foreign experts for further inspection of the Polygon. With their help, it will be necessary to justify the scientific and technical complex of rehabilitative and protective measures to minimize the migration of HCB residues beyond the Polygon site.

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PROBLEMS OF DIOXIN POLLUTION “HOT POINTS” IN RUSSIA

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Abstract

The paper makes assessment of the current state of preparation for rehabilitation of the dioxin pollution “hot point” in Ufa, Russia. Bottlenecks of the Russian legislation in the field of regulation of POPs maximum content are lightened, which is necessary for making basic decisions on cleanup measures concerning polluted soil, building material, communications, etc. An example of calculation of dioxin-containing waste hazard carried out according to the main regulation document – the Order of the Ministry of Natural Resources of the Russian Federation No. 511 “On setting criteria for relating waste to a class of hazard” is given.

Keywords

Waste, POPs, dioxins, rehabilitation, limits of clearance, “hot points”.

Ratification of the Stockholm Convention by the Russian Federation in 2011 has not yet sufficiently prompted the

activity in the field of cleanup of POPs polluted areas. In 2010, a project of the National Plan for realization of terms of the Stockholm Convention in the Russian Federation was presented. The source information for it was the analysis of available separate data on studies in the field of POPs and the experience of the estimated dioxin inventory carried out in Russia in 2007. It was calculated that dioxin emission into the air from different sources in Russia makes 1784.4 g TEQ PCDD/Fs. The largest contribution into the total dioxin emission is made by burning solid waste landfill sites (35.3%), ferrous and non-ferrous metallurgy (28.3%) and building material industry (13.6%). The share of chemical industry is assessed as 0.02% (!), and burning of hazardous waste – 6.72% [1].

Besides emission from stationary sources, there are dioxin polluted areas with high dioxin concentration formed due to the production of chlorophenol products,

2,4,5-T, 2,4-D and others. Most known dioxin polluted areas are in the regions of the Ural and Povolzhje, these are the plants of the net “Khimprom” in Ufa and Chapayevsk. Pollution levels of the plant territory in Ufa make about 10 ppb in the materials of buildings, to 6 ppb in soil and reach 200 ppb in slit and sludge [2]. Some of these plants have been shut down, in Chapayevsk – from 2000, in Ufa from 2004 after a bankruptcy procedure.

Now these territories present by themselves gradually dilapidating buildings with dismantled and removed equipment, and it is unknown whether cleanup from dioxins was carried out or not. In Ufa, this process has resulted in “liquidation” of the most polluted shops by their destruction and storing building breakage in a new place within the same area (Figures 1, 2).



Figure 1: The building of the shop where phenoxyherbicides were produced with incineration furnace for chlororganic waste burning prepared for destruction

As this process was going on without following the norms of protection against spreading of polluted particles with high dioxin content (1-15 ppb), the results were clearly traced by the level of snow cover pollution [3].

In the Russian Federation, the projects on liquidation of accumulated environmental damage of the past years had been developed.

These projects were included into the program “Environmental Safety of Russia”, the realization of which began in 2013.

For the plant in Ufa, a project of liquidation of the dioxin pollution “hot point” was developed. It is supposed that reclamation of the “Khimprom” territory will take over two

billion rubles. The Ministry of Natural Resources of the Russian Federation obliged itself to include this plant into the program of 2014 in priority order. In Chapayevsk, the work on development of a program for rehabilitation of the polluted territory also began.

However, the present state of affairs is complicated by unpreparedness of the legislative and regulatory basis in Russia for making management and technical decisions on clearance. There are no norms of maximum dioxin content in soil of residential areas (interim standards of dioxin in soil make 0.33 pg/g), there are no MAC in the air of the working zone, permissible emissions from incineration furnaces are



Figure 2: Storing of building breakage of destroyed buildings, 2013

not regulated (in some studies EU norms of 0.1 ng/m³ are used).

However, the main problem is the absence of the notion “the limit of clearance” for soil, waste, sludge and building materials polluted by dioxins. The calculation of hazard of sludge as waste carried out according to the criteria adopted in Russia refer the waste containing dioxin (and other POPs) over 1 ppb to IV or even to V class of hazard (practically to non-hazardous, at the level of domestic waste) because of low absolute concentrations.

Thus the Order of the Ministry of Natural Resources of the Russian Federation No. 511 “On setting of criteria for relating hazardous waste to a class of hazard for the environment” contains the method of assessment of waste hazard by calculation of the hazard factor K. Five classes of hazard are singled out (Table 1).

The factor of the degree of waste hazard to the environment **K** is calculated by the following formula: **K = K₁ + K₂ + + K_n**, where **K** – factor of the degree of waste hazard to the environment;

K₁, K₂,K_n – factors of the degree of hazard of separate components of waste to the environment.

Degree of hazardous impact of waste	Criteria of relating hazardous waste to a class of hazard for the environment	Class of hazard of waste for the environment
Very High	The environmental system is irreversibly deteriorated. There is no period of reclamation	Class I Extremely hazardous
High	The environmental system is strongly deteriorated. The reclamation period is no less than 30 years after the total liquidation of the source of hazardous impact	Class II Highly hazardous
Middle	The environmental system is deteriorated. The reclamation period is no less than 10 years after reducing hazardous impact of the existing source	Class III Moderately hazardous
Low	The environmental system is deteriorated. The period of self-recovery is no less than 3 years	Class IV Low-hazard
Very low	The environmental system practically is not deteriorated	Class V Practically non-hazardous

Table 1: Classification of hazardous waste in Russia

The factor of the degree of hazard of a waste component to the environment **K_i** is calculated by the formula: **K_i = C_i / W_i**, where

C_i – the concentration of the i-th component in the waste (mg/kg waste);

W_i – factor of the degree of hazard of the i-th component of the waste to the environment (mg/kg waste).

Relation of waste to a class of hazard is proposed to be carried out by calculation and/or experimental methods.

19 indicators are used that characterize the degree of hazard of every component to different natural environments. Relation of the waste to a class of hazard by the calculation method according to the indicator of the degree of the waste hazard to the environment is performed in compliance with Table 2.

Some of the given values of factors of the degree of hazard (W_i) including “dioxins” are given in Table 3. Thus for “dioxins” this value makes 24.6 mg/kg, there are also “furans” for which this value is considerably higher - 359 mg/kg. Application of this method to the waste containing dioxins at the level of 1 ppb TEQ PCDD/Fs (1000 ng/kg) results in the value $K_{PCDD/F} = 4 \cdot 10^{-6}$ and actually cannot influence the total value taking into consideration other components of the dioxin-containing waste (for example, wall plaster).

There are still more question to the methods. Thus it is unclear whether TEQ value is used in calculations or concentrations of congeners PCDD and PCDF.

So to be related to the 1st class of hazard a dioxin-containing waste should contain 250 g TEQ PCDD/Fs in 1 kg of waste.

With evident unacceptability it was namely this method that was used to assess the hazard of building waste from destroyed shops and waste in sludge tanks.

Class of hazard of waste	Degree of hazard of waste to the environment (K)
I	$10^6 \leq K < 10^4$
II	$10^4 \leq K < 10^3$
III	$10^3 \leq K < 10^2$
IV	$10^2 \leq K < 10$
V	$K \leq 10$

Table 2 :Classification of waste by degree of hazard

Name of component	W_i , mg/kg
Aldrin	138
Benz(a)pyrene	59.97
Hexachlorbenzene	354
Dioxins	24.6
Dichlorphenol	39.8
Dichlordiphenyltrichlorethane	213.8
Lindane	4634
Pentachlorbiphenyls	59.98
Pentachlorphenol	75.85
Trichlorbenzene	598.4
Phenol	215.44
Furans	359
Chloroform	215.4

Table 3: Factors of the degree of hazard

Besides the calculation method, the Order No. 511 gives an experimental method of assessment based on biological testing. Reaction of daphnia and/or water plants on water extract of waste sample is used. The method is a priori unsuitable for PCDD/Fs due to their extremely low solubility.

The way out, to our opinion, is excluding POPs from the list of waste, to which the effect of the document is applied, as it was done with radioactive and medicine waste.

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NEW LISTED POPs IN THE STOCKHOLM CONVENTION AND GUIDANCES DEVELOPED FOR THE UPDATE OF THE NATIONAL IMPLEMENTATION PLAN

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The Stockholm Convention on Persistent Organic Pollutants (POPs; <http://chm.pops.int>) is an international treaty aimed at protecting human health and the environment from the threats posed by POPs. The Convention goals are to restrict and ultimately eliminate the production, use, release, and stockpiles of POPs.

The Convention also establishes regulation on the international trade of POPs and their disposal upon becoming wastes. An initial twelve POPs were listed under the Convention when it was adopted in 2001.

The Conference of the Parties (COP) to the Stockholm Convention decided to list nine new chemicals in 2009 (alpha-HCH, beta-HCH; gamma-HCH/Lindane, commercial pentabromodiphenylethers (major compositions are tetra- and penta-homologues) and commercial octabromodiphenylethers (containing hexa-, and hepta-homologues); PFOS, its salts, PFOSF and PFOS related chemicals, Chlordecone and pentachlorobenzene).and additional

chemicals in 2011 (Endosulfan) and 2013 (Hexabromocyclododecane (HBCD)). Therefore for the first time brominated and fluorinated chemicals have been listed which are used as industrial chemicals largely in consumer goods and for PFOS additionally in a range of industrial applications.

To assist Parties in updating their National Implementation Plans (NIPs) to address the new listed POPs listed in 2011, a set of guidance documents has been developed by the United Nations Industrial Development Organization (UNIDO) and the United Nations Institute for Training and Research (UNITAR), working in collaboration with the Secretariat of the Stockholm Convention (SSC) and the Global Environment Facility (GEF). These documents aim at supporting Parties in developing strategies to restrict and eliminate the new listed POPs, by providing guidance on establishing inventories and selecting Best Available Techniques and Best Environmental Practices (BAT and

BEP) for situations when production, use, and recycling of industrial POPs are allowed by the Convention.

The following guidance documents (several of them still drafts needing approval by COP) have been prepared to assist parties with National Implementation Plan review and update and can be downloaded from the Stockholm Convention website¹ :

1. Guidance for developing, reviewing, and updating a NIP for the Stockholm Convention on POPs.
2. Guidance for the inventory of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention on POPs
3. Guidance for the inventory of polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on POPs

¹<http://chm.pops.int/Implementation/NIPs/Guidance/tabid/2882/Default.aspx>

4. Guidance for the Inventory of commercial Pentabromodiphenyl ether (c-PentaBDE), commercial Octabromodiphenyl ether (c-OctaBDE) and Hexabromobiphenyls (HBB) under the Stockholm Convention on Persistent Organic Pollutants; Draft.

5. Guidelines on best available techniques and best environmental practices for the production and use of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention on POPs

6. Guidelines on BAT and BEP for the recycling and waste disposal of articles containing polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on POPs

7. Guidance for the control of the import and export of POPs

8. Labelling of products or articles that contain POPs – Initial considerations

9. Guidance on Sampling, Screening and Analysis of Persistent Organic Pollutants in Products and Articles; Draft;.

10. Guidance on calculation of action plan costs for specific POPs

In addition technical guidelines have been developed by the Basel Convention. addressing new listed POPs including:

1) Draft technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with hexabromodiphenyl ether and heptabromodiphenyl ether, and tetrabromodiphenyl ether and pentabromodiphenyl ether (POP-BDEs).

2) Draft technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF).

Fourth Draft. 26. November 2014.

Also other publications and materials have been developed for an overview on new listed POPs such as the “Step-by-step companion guide to the review and updating of the National Implementation Plans – 2011” or “STARTUP GUIDANCE for the 9 new POPs” and can be downloaded from the Convention Website².

An important activity for the National Implementation Plan update is the development of inventories of the new listed POPs which are then the basis for the development of action plans.

² <http://chm.pops.int/Implementation/NewPOPs/Publications/tabid/695/Default.aspx>

THE UPDATED “TOOLKIT FOR IDENTIFICATION & QUANTIFICATION OF RELEASES OF DIOXINS, FURANS AND OTHER UNINTENTIONAL POPs UNDER ARTICLE 5 OF THE STOCKHOLM CONVENTION POPs”

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One major goal of the Stockholm Convention on Persistent Organic Pollutants (POPs) is the continuing minimization and, where feasible, ultimate elimination of unintentionally produced POPs including polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDF), unintentionally formed polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB) and pentachlorobenzene (PeCBz) (Article 5). Parties are required to identify, characterize, quantify and prioritize sources of releases of unintentionally produced POPs, and develop strategies with concrete measures, timelines and goals to minimize or eliminate these releases (Stockholm Convention 2013).

To support Parties in meeting these obligations, a “Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases” was first published in 2003 by UNEP and revised in 2005. The toolkit ensures that source inventories and release estimates are complete, transparent, as well as consistent in format

and content. The Toolkit allows Parties to compare results, identify priorities, mark progress and follow changes over time at the national, regional and global levels (Fiedler et al. 2012; Stockholm Convention 2013).

In 2006, Parties acknowledged the need for its ongoing revision and updating, placing emphasis on key sources for which limited data were available and on providing support to developing countries in their efforts to verify their emission factors. This updated version has meanwhile been developed and has been released early 2013.

The revision process was open and inclusive, involving experts nominated by Parties as well as by nongovernmental organizations and industry associations, and in cooperation with UNEP Chemicals.

The Toolkit is the most comprehensive available compilation of emission factors for the relevant PCDD/PCDF sources. It is useful particularly in countries where

measurement data are limited or are not available, enabling the elaboration of source inventories and release estimates by using the default emission factors. It is also useful in countries where national measurement data are available, as a reference document for data comparison and validation purposes.

The 2013 edition of the Toolkit contains all new information, as well as model inventories illustrating relevant releases. In addition, the entire Toolkit is now available in an interactive electronic version online (<http://toolkit.pops.int/>), with information structured according to the level of technical detail.

The presentation gave a short introduction to the updated 2013 toolkit and an overview on the NIP update process for unintentionally produced POPs.

References

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Stockholm Convention (2012) Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention on Persistent Organic Pollutants.

Ren Z, Zheng M (2009) Impacts of human activities on dioxins emissions at national scale. *Chemosphere* 76, 853–859.

NEWLY LISTED POPS AND OTHER STOCKHOLM CONVENTION ISSUES

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The presentation of Roland Weber (POPs Environmental Consulting) introduced the recent developed The Stockholm Convention guidance drafts for the inventory development and for BAT/BEP management of perfluorooctanesulfonic acid (PFOS) and polybrominated diphenylethers (PBDEs) recently listed in the Stockholm Convention.

Timo Seppala (Finnish Environment Institute) gave an overview on the key issues of the most recent Stockholm Convention listed substance: hexabromocyclododecane (HBCD).

Mihaela Claudia Păun (Ministry of Environment and Climate Change, Romania) gave an insight into the approach of Romania to update the National Implementation Plan (NIP) with emphasise on the new listed POPs.

Ivan Holoubek (RECETOX, Czech Republic) made an overview on the “Global POPs monitoring and an insight into the current state in the CEE countries”. In ad-

dition, he made a critical evaluation of the effectiveness of the Stockholm Convention measures.

The last part of the session focused on dioxins and other unintentionally produced POPs. Roland Weber gave an overview of the “Updated toolkit for identification and quantification of releases of dioxins and other unintentional POPs in the Stockholm Convention” with the emphasis on the contaminated sites chapter. The last two presentations gave some details on the two examples of contaminated megasites with dioxins and unintentionally produced POPs:

Zarema Amirova (Environmental Research & Protection Centre, UFA, Russia) gave an overview of the problems of dioxin contaminated sites in UFA. Georgii Lysychnenko (Director of Institute of Environmental Geochemistry, Ukraine) gave a status report on the current situation and the waste management of the HCB waste stockpile in Kalush/Ukraine.

Overall, the session provided a good insight on the key issues on new listed brominated and fluorinated POPs and also on the contaminated site challenges of Dioxins and other unintentionally formed POPs. Therefore, the session complemented other sessions (focusing largely on pesticides issues) and brought to the Conference a more comprehensive picture on the POPs challenges the world and, in particular, the countries in this region are facing.

Further reading

Guidance documents prepared to assist parties with National Implementation Plan review and update and can be downloaded from the Stockholm Convention website <http://chm.pops.int/Implementation/NIPs/Guidance/tabid/2882/Default.aspx> Stockholm Convention (2013) Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention POPs. <http://toolkit.pops.int/>