BRATISLAVA MAY 29–31, 2013

INTERNATIONAL CONFERENCE

CONTAMINATED SITES BRATISLAVA 2013

CONFERENCE PROCEEDINGS

Agenda

INTERNATIONAL CONFERENCE
CONTAMINATED SITES BRATISLAVA 2013

Ministerstvo životného prostredia Slovenskej republiky

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EURÓPSKA ÚNIA

BRATISLAVA May 29 –31, 2013

Nr	Time	Presenter Name Surname (Country)	Presentation Title
	MAY 30, 2013 8:00– 8:50	**Registration**	
	8:50–10:40	**Session 1**	
		Chairman: Mrs. Jánová /Mr. Andersen	
0	**8:50–9:00**	**Ministry of Environment of the SR**	WELCOME SPEACH
1	9:00–9:20	**Marijke Cardon (B)**	THE SOIL PROTECTION AT EU-LEVEL
2	9:20–9:40	**Vlasta Jánová (SK)**	IMPLEMENTATION OF THE LAW ON CONTAMINATED SITES IN SLOVAKIA
3	9:40–10:10	**Sophie Capus (L)**	INVENTORIES AND REGISTERS OF CONTAMINATED SITES/STATE OF THE SITUATION
4	10:10–10:40	**Esther Goidts (B)**	INVENTORIES AND REGISTERS OF (POTENTIALLY) CONTAMINATED SITES – IMPLEMENTATION IN WALLONIA (BELGIUM)
	10:40–11:00	**COFFEE BREAK**	
	11:00–12:40	**Session 2**	
		Chairman: Mrs. Darmendrail/Mr. Vegter	
5	11:00–11:20	**Paul Nathanail (GB)**	RISK BASED SUSTAINABLE REMEDIATION
6	11:20–11:40	**Moritz Ortmann (A)**	IMPLEMENTING SUSTAINABILITY INTO REMEDIATION – – THE AUSTRIAN WAY
7	11:40–12:00	**Markus Ausserleitner (A)**	TOWARDS A NEW CONTAMINATED SITES ORDINANCE ESTABLISHING COMPREHENSIVE ASSESSMENT CRITERIA IN AUSTRIA
8	12:00–12:20	**Jorge Santos Garcia (P)**	A STRATEGY TO DEFINE LEGISLATION ON SOIL CONTAMINATION – THE PORTUGUESE EXAMPLE
9	12:20–12:40	**Zdeněk Suchánek (CZ)**	CONTAMINATED SITES INVENTORY PROJECT IN THE CZECH REPUBLIC – METHODOLOGY OUTLINES
	12:40 – 13:40	**LUNCH**	
	13:40 – 15:20	**Session 3**	

	Time	Presenter Name Surname (Country)	Presentation Title
Chairman: Mrs. Cardon/Mr. Nathanail			
10	13:40–14:00	**Dragana Vidojević (SRB)**	INVENTORY OF CONTAMINATED SITES IN SERBIA
11	14:00–14:20	**Jiří Tylčer (CZ)**	CONTAMINATED SITES IN THE CZECH REPUBLIC – GENERALISATION OF RESULTS FROM TRIAL INVENTORY OF PILOT AREAS
12	14:20–14:40	**Antonella Vecchio (I)**	RISK PRIORITIZATION AND RISK ASSESSMENT AS A TOOL FOR MANAGING CONTAMINATED SITES
13	14:40–15:00	**Maria S. Kuyukina (RUS)**	MANAGEMENT OF CRUDE OIL CONTAMINATED LAND IN RUSSIA USING A RISK ASSESSMENT APPROACH
14	15:00–15:20	**Laura D'Aprile (I)**	THE ROLE OF NATURAL ATTENUATION IN THE RISK ANALYSIS FRAMEWORK
	15:20–15:40	**COFFEE BREAK**	
	15:40–17:00	**Session 4**	
Chairman: Mr. Kasamas/Mrs. Wepner-Banko			
15	15:40–16:00	**Iason Verginelli (I)**	A NEW SOFTWARE (RISK-NET) FOR THE APPLICATION OF RISK ASSESSMENT TO CONTAMINATED SITES
16	16:00–16:20	**Agnieszka Klimkowicz-Pawlas (PL)**	ECOLOGICAL RISK ASSESSMENT FOR SOILS CONTAMINATED WITH PAHS – TREATS TO SOIL HABITAT FUNCTION
17	16:20–16:40	**Zokir Rahimov (UZ)**	OBSOLETE PESTICIDES TECHNICAL STUDY AND CONTAMINATED SITE REMEDIATION IN THE REPUBLIC OF UZBEKISTAN
18	16:40–17:00	**Valentin Plesca (MD)**	INVENTORY OF POP PESTICIDES POLLUTED AREAS IN MOLDOVA
	17:00 – 17:30	**DISCUSSION**	
	19:00 – 22:00	**GALA DINNER**	

Nr	**Time**	**Presenter Name Surname (Country)**	**Presentation Title**
	MAY 31, 2013 8:00–8:10		**Registration**
	8:10–9:50		**Session 5**
			Chairman: Mrs. Dercová/Mr. James
19	8:10–8:30	**Jiří Mikeš (CZ)**	ALTERNATIVE APPROACHES IN BIOREMEDIATION ENGINEERING
20	8:30–8:50	**Kevin Helps (HU)**	THE FAO ENVIRONMENTAL MANAGEMENT TOOL KIT VOLUME 5; A SYSTEMATIC AND PRAGMATIC FRAMEWORK FOR DEALING WITH PESTICIDE CONTAMINATED LAND PROBLEMS FOR USE IN LOW TO MIDDLE INCOME COUNTRIES
21	8:50–9:10	**John Keith (USA)**	RAPID ASSESSMENT OF POPS PESTICIDE CONTAMINATION SITES – A SIMPLIFIED METHOD AND INNOVATIVE DATA MANAGEMENT SYSTEM DEVELOPED FOR VIETNAM
22	9:10–9:30	**Ion Barbarasa (MD)**	REMEDIATION OF POP PESTICIDES POLLUTED AREAS IN THE CONDITIONS OF MOLDOVA
23	9:30–9:50	**Katarína Dercová (SK)**	BIOSTIMULATION AND BIOAUGMENTATION – – TWO PROSPECTIVE STRATEGIES OF ADVANCED BIOREMEDIATION TECHNOLOGIES
	9:50–10:20		**COFFEE BREAK**
			Session 6
			Chairman: Mr. Tylčer/Mr. Ortmann
24	10:20–10:40	**Trystan James (UK)**	BROFISCIN QUARRY REMEDIATION SCHEME, CARDIFF, WALES
25	10:40–11:00	**Peter C. Stanley (UK)**	BROFISCIN QUARRY REMEDIATION SCHEME, CARDIFF, WALES
26	11:00–11:20	**Katarína Földešová (SK)**	MAJOR MILESTONES AND ACCOMPLISHMENTS OF REMEDIATION AT LOGISTICS SITES IN SLOVNAFT, a. s.
27	11:20–11:40	**Grzegorz Siebielec (PL)**	PERSISTENCE OF SMELTER WASTELAND PHYTOREMEDIATION – LESSONS FROM LONG TERM FIELD TESTING
28	11:40–12:00	**Ľubica Palkovičová (SK)**	ENVIRONMENTAL EXPOSURE TO ENDOCRINE DISRUPTORS AND SELECTED METABOLIC MARKERS IN CHILDREN
	12:00–13:00		**LUNCH**
	13:00 – 17:00		**FIELD TRIPS**

SOIL PROTECTION AT EU-LEVEL

Eddy Van Dyck[1] – **Marijke Cardon**[2]

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KEYWORDS
Europe, legislation, soil protection, industrial emission, ...

ABSTRACT

Soil is defined as the top layer of the earth's crust. The interface between the earth, the air and the water, soil is a non-renewable resource which performs many vital functions: food and other biomass production, storage, filtration and transformation of many substances including water, carbon, nitrogen. Soil has a role as a habitat and gene pool, serves as a platform for human activities, landscape and heritage and acts as a provider of raw materials. These functions are worthy of protection because of their socio-economic as well as environmental importance.

Erosion, loss of organic matter, compaction, salinisation, landslides, contamination, sealing… Soil degradation is accelerating, with negative effects on human health, natural ecosystems and climate change, as well as on our economy. At the moment, only nine EU Member States have specific legislation on soil protection (especially on contamination).

Different EU policies (for instance on water, waste, chemicals, industrial pollution prevention, nature protection, pesticides, agriculture) are contributing to soil protection. But as these policies have other aims and other scopes of action, they are not sufficient to ensure an adequate level of protection for all soil in Europe.
For all these reasons, the Commission adopted a Soil Thematic Strategy on 22 September 2006 with the objective to protect soils across the EU.

THE SOIL THEMATIC STRATEGY

The Thematic Strategy for Soil Protection consists of a Communication from the Commission to the other European Institutions, a proposal for a framework Directive (a European law), and an Impact Assessment.The Communication explains why further action is needed to ensure a high level of soil protection, sets the overall objective of the Strategy and explains what kind of measures must be taken. It establishes a ten-year work program for the European Commission.

The proposal for a framework Directive sets out common principles for protecting soils across the EU. Within this common framework, the EU Member States will be in a position to decide how best to protect soil and how use it in a sustainable way on their own territory.

The Impact Assessment contains an analysis of the economic, social and environmental impacts of the different options that were considered in the preparatory phase of the strategy and of the measures finally retained by the Commission.

DECISION MAKING PROCESS

The Soil Thematic Strategy takes the form of a Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee, and the Committee of the Regions. It is not a legislative proposal and is therefore not subject to a formal process of adoption.

The proposal for a Soil Framework Directive is subject to the co-decision procedure in accordance with Article 251 of the EC Treaty. This means that both the European Parliament and the Council have to agree on a common text on the basis of a proposal from the Commission and taking into account the opinions of the Committee of the Regions and the European Economic and Social Committee.

Despite the efforts of several Presidencies, the Council has so far been unable to reach a qualified majority on this legislative proposal due to the opposition of a number of Member States constituting a blocking minority. The latest discussions during the Spanish Presidency (first half of 2010) have not changed this situation.

OTHER EUROPEAN LEGISLATION RELEVANT FOR SOIL PROTECTION

Renewable Energy Directive, Landfill Directive, Environmental Liability Directive, Water Framework Directive, Guidelines for State Aid, Waste Framework Directive,... are only a handful of the European (environmental) directives which can be linked with soil protection. The most recent directive with a significant link to soil contamination and remediation is the Industrial Emission Directive.

INDUSTRIAL EMISSION DIRECTIVE

Specific to soil, the Industrial Emission Directive (IED) increases the importance of prevention and monitoring of soil contamination. IPPC activities with the use, production or release of relevant hazardous substances, have specific provisions imposed on potential emissions to soil. These provisions include the entire life cycle of the IPPC installations: 1) for the commencement of the operation a situation report, 2) during the operation a minimum periodic monitoring, and 3) by cessation of activities an investigation and possible remediation. New activities should prior to the start of the operation, conduct a situation report (also called baseline report) of the soil and groundwater so that subsequent at closure a quantified comparison can be made. This baseline report shall contain information on the state of soil and groundwater contamination. It should also inquire about the current and past uses of the site. Europe demands that potential soil and groundwater contamination is periodically checked, or at least every ten and five years. The Directive allows a different frequency based on a systematic appraisal of the risk of contamination.

LITERATURE

Website European Commission – DG Environment – Unit Soil
Website OVAM

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IMPLEMENTATION OF THE LAW ON CONTAMINATED SITES IN SLOVAKIA

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ABSTRACT

Act No. 409/2011 Coll. on some measures in the field of contaminated sites and on amendments to certain laws came into force on January 1, 2012. The Act focuses on identification and classification of contaminated sites, defines the originator and the body liable for the contaminated site and their obligations, establishes a procedure if a liable body cannot be determined, defines the working plan for contaminated site remediation and the way of its completion and operation of state authorities in the field of contaminated sites. Adoption of the Act is an important step towards the systematic removal of contaminated sites in Slovakia. The first year of implementation of the Act has the first positive results.

INTRODUCTION

The most important activities of the Ministry of the Environment of the Slovak Republic in the previous period include the project of Systematic Inventory of Contaminated Sites in Slovakia (2006 - 2008), creation of Information System of Contaminated Sites (2008 – 2010),
approval of the State Programme of Contaminated Sites Remediation (2010 – 2015) by the Slovak Government in March 2010 and implementation of the Operational Programme Environment Slovakia 2007-2013.

In October 2011, the National Council of the Slovak Republic approved the Act No. 409/2011 Coll. on some measures in the field of contaminated sites and on amendments to certain laws. The Act came into force on January 1, 2012 and brought new conditions for systematic tackling of environmental burdens from the past. The first year of implementation of the law was filled with creation of state administration on this issue, identification of new environmental burdens reported by professionals and public, updating information system of contaminated sites, determining the responsible persons and the first approval of the Working Plans for contaminated site remediation. In synergy with the geological legislation, the Ministry of the Environment of the Slovak Republic established the Commission for Consideration and Approval of Final Reports with Risk Analysis.

Creation of state administration in the field of contaminated sites

Bodies of state administration in the field of contaminated sites include:

a) Ministry of the Environment of the Slovak Republic,
b) Regional Environmental Offices and
c) Slovak Environmental Inspectorate.

In order to instruct the staff of the Regional Environmental Offices, the Ministry of the Environment elaborated two methodological instructions and a methodological guideline:

- Methodological instruction of the Ministry of the Environment of the Slovak Republic for determination of liable person under the Law No. 409/2011 Coll. on some measures in the field of contaminated sites and on amendments to certain laws,
- Methodological instruction of the Ministry of the Environment of the Slovak Republic for the Working plans for contaminated site remediation under the Law No. 409/2011 Coll. on some measures in the field of contaminated sites and on amendments to certain laws.
- Methodological guideline No. 1/2012-7 on risk analysis of polluted site.

In 2012, the Ministry of the Environment in cooperation with the Slovak Environmental Agency, organized 9 special trainings, where more than 250 civil servants and 80 employees of private sector were trained on the issue of the new law.

Identification of contaminated sites

According to the law, anybody who suspects the presence of contamination in the country may inform the Ministry of the Environment or the Regional Environmental Office. Information can be submitted in a paper form, an electronic form or orally. The Ministry of the Environment makes sure whether the site is really contaminated, if so, it completes a registration form, classifies it and ensures its entry into the Information System of Contaminated Sites.

In this way, there were 63 suspicious sites audited in 2012. Ten of them were identified as probable contaminated sites and localities and were entered into the information system. Identification of contaminated sites and updating of information system are performed by the Slovak Environmental Agency.

Responsibility for contaminated sites

The law provides a way of determining the responsible body for the contaminated site and according to the polluter pay principle introduces a definition of an originator of the contaminated site. The originator is anyone, who by his activities has caused contamination. The originator is directly responsible for the contaminated site remediation. If the originator folded up (the company no longer exists) or died (if an individual), the Regional Environmental Office determines in the proceedings that a legal successor or a property owner may be responsible for the contaminated site remediation. In 2012, there were 37 proceedings initiated, 31 of them were finished.

Relevant ministry

If a body or a person liable for the contaminated site cannot be determined, the procedure is stopped and the Government of the Slovak Republic decides which ministry shall assume responsibilities of the responsible person and manage the remediation. In April 2013, the Slovak Government adopted the Resolution No. 150/2013, where the Ministry of the Environment and the Ministry of the Defence were entrusted with the management of the remediation of 19 contaminated sites.

Working plan for contaminated site remediation

The Working Plan for contaminated site remediation represents the basic planning document, which should be submitted for approval to the Regional Environmental Office. Up till now, more than 20 of them have been submitted. After the approval, the working plans will be included in the Information System of Contaminated Sites and will be available to the public.

CONCLUSION

The Act on some measures in the field of contaminated sites has created special conditions for further progress of works in this field and allows to remove barriers that make impossible to remediate contaminated sites. The importance of the Act is also unquestionable for EU funds drawing, where Slovakia has a long delay. Based on above mentioned information on implementation of the Act during the first year of its existence, we can briefly summarize that the Act on contaminated sites appears to be viable and useful and set conditions will bring benefit for all of us and also for future generations.

INVENTORIES AND REGISTERS OF (POTENTIALLY) CONTAMINATED SITES – IMPLEMENTATION IN WALLONIA (BELGIUM)

Esther Goidts[1] **– Arnaud Warin**[1] **– Maxime Semer**[1]

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KEYWORDS
Inventories, (potentially) contaminated sites, databases, mapping, soil investigations, remediation cost

ABSTRACT

Inventories of potentially contaminated sites rely on various databases, often arising from legal obligations. Therefore, the first steps of making such inventories involve to gather thematical databases in order to analyse their synergy. This requires to evaluate the relevance and the resolution of each database, as well as the technical feasibility of their integration, given a referential framework not only based on a common terminology (e.g. definition of potentially contaminated sites) but also on a common spatial resolution in order to consistently characterize each site through time and space.

In Wallonia, potentially contaminated sites are defined as sites where potentially contaminating activities take or took place. One „site“ refers to the ensemble of adjacent or contigues cadastrial parcels covered by the activity and its various installations. The potentially contaminated activities/installations are defined in the Annex III of the Soil decree (231 activities/installations are identified). The first legal databases available concerning such sites relate to waste and land planning decrees in the eighties, then environmental legislations from the late nineties added more exhaustive databases (see Table 1). The current number of potentially contaminated sites ranges from 3439 to 17.009 sites, which corresponds to an average density of 2 to 10 sites per 10 km². This reflects the industrial past of Wallonia, where coal and metal (iron) mining developped increasingly in the 18th and 19th century, such that Wallonia became the second world industrial power in the 19th century. Most of the potentially contaminated sites are therefore economic wasteland including brownfields, and later on gas stations became also a significant part of these sites. Between two third or one eighth (given respectively the low or high estimates – Table 1) of the potentially contaminated sites identified were already found contaminated following soil investigations, with more than half of them now remediated. Provided that relevant historical data are available, numerous potentially contaminated sites can also be identified (5694 sites found on the Vandermaelen map), although duplicates may be found due to successive activities taking place on the same location.

Tab. 1. Number of (potentially) contaminated sites according to the different available databases (from ICEW, 2012)

Legal framework / Driver	**Starting date of database**	**n sites**		**Potentially contaminated**		**Contaminated**	**Remediated**
		low estimate	high estimate	low estimate	High estimate		
Soil decree	5/12/2008	62	62			62	0
Environmental permit decree	11/3/1999	419	5765	419	5765	0	0
Protection at work – gas stations	4/3/1999	2006	2286	1310	1590	429	267
Waste decree	1985 - 26/6/1996	1301	1301	368	368	255	678
Economic wasteland (brownfields included) within land planning decree	1978 - 27/11/1997	1967	4217	1342	3592	248	377
Historical studies (Vandermaelen map – CHST 2012)	*1846 - 1854*	*0*	*5694*	*0*	*5694*		
Total		***5.755***	***19.325***	***3.439***	***17.009***	***994***	***1322***

With the approuval of the specific legal framework dealing with soil management (Soil Decree, mainly focused on contaminated sites), the integration of the different databases has started, raising the issue of mapping the different databases within the cadastrial parcel reference framework. Indeed, prior to the year 2000, the databases were only used for basic administrative management within separated legal framework and without mapping considerations (only the site address was recorded with possibly a local map). However, as mapping allows to proceed an integrated approach for soil management and allows to systematically identify potential duplicates between databases, provided that a consistent spatial reference is used, this spatial work started and is currently under progress.

Three types of databases can be distinguished when dealing with database georeferencing: i) exhaustive georeferenced database easily available and rapid to integrate into a centralised database (cadastrial matrix, existing databases of contaminated sites, ...); ii) database requiring a pre-process in order to extract potentially polluting activities and to digitise cadastrial parcels (environmental permits database, historical database, ...); iii) database presenting difficulties for further integration (no detailed georeferencing available, restricted access,...). Figures 1 and 2 illustrate the work done on digitalisation of old potentially polluting activities and their spatial extent from the historical Vandermaelen map (edited between 1846 and 1854 at a 1/20.000 scale) and adjusted to the current geodataframe used for cadastrial parcels.

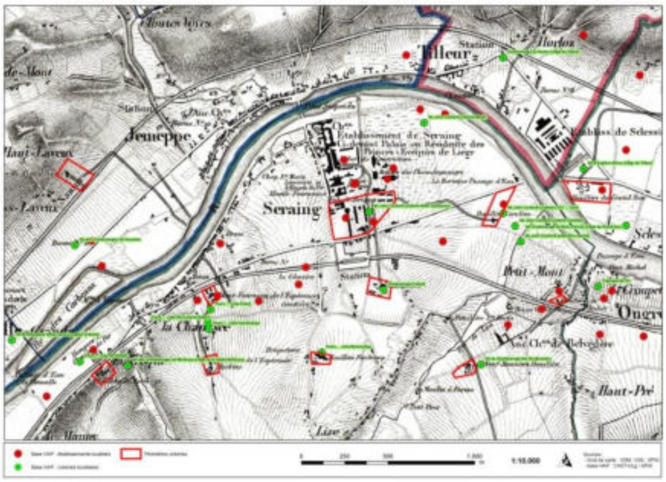

Fig. 1. Identification of sites where potentially contaminating activities occured on the Vandermaelen map edited around 1850 (from CHST, 2012)

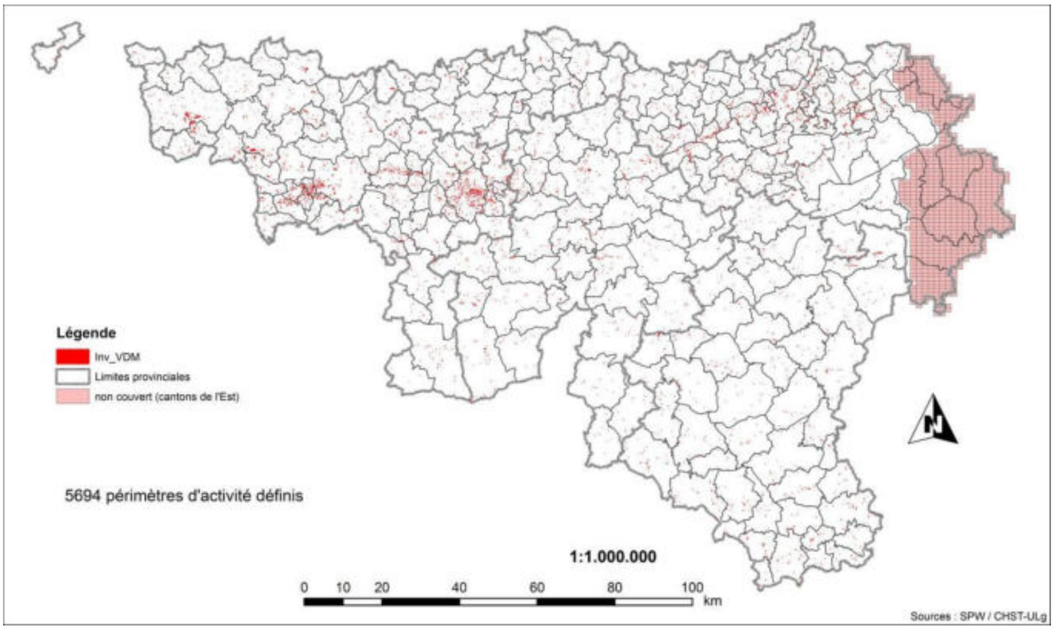

Fig. 2. Sites where potentially contaminating activities occured in 1850 in Wallonia (from CHST, 2012)

The updated inventory of potentially contaminated sites based on the current spatial integration of each database will then be used as a driver for detailed soil investigations by accredited soil experts within the Soil Decree framework. Indeed, different legal triggers are defined for starting investigations on sites where potentially contaminating activities have taken or are taking place: administrative and voluntary procedures, permit demand, bankruptcy, end of activity and environmental damage. Purshase was initially forseen as a trigger for soil investigation obligations, but is being reconsider within a voluntary procedure that may arise from the legal obligation of notaries to inform the seller and the buyer on the status of the soil following a consultation of the map of potentially contaminated sites issued by the administration.

The system of triggers for soil investigations is therefore a dynamic system through time, which differs from a systematic approach for identification and subsequent remediation of contaminated sites. The polluter – payer principle is applied such that soil investigations and remediation costs are supported by the private sector. However, in addition to this trigger system, a number of orphan sites have to be handled through the public channel. In that second system, contaminated sites are prioritised within a public remediation plan for which budget is approved by the government. It is therefore an amount of 369 M€ that have been recently allocated to the remediation of 60 priority contaminated brownfield and economic wasteland, and 205 M€ to the investigation and, if necessary, rehabilitation of 176 priority less or uncontaminated brownfield and economic waste land (ICEW, 2012).

In conclusion, implementation of inventories of (potentially) contaminated sites is crucial for soil management and land planning, but requires important efforts of databases gathering, georeferencing, and cleaning in order to have an integrated mapping of such sites. Historical data can be of high relevance, but depend on the quality of the information (identification of activities and their location). The adequate resolution of such inventory (at least for Wallonia) is the cadastrial parcel in order to avoid duplicates through space, to trace back the succession of activities through time, and to identify the potential responsible of obligations. Work is in progress to reach such resolution for each database available, while priority brownfield and economic wasteland are being under remediation through public supported funds.

LITERATURE

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IMPLEMENTING SUSTAINIBILITY INTO REMEDIATION – THE AUSTRIAN WAY

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KEYWORDS
Ecological-economic assessment; Modified Cost-Effectiveness-Analysis (MCEA); hierarchy of goals; ecology; local development; project stability

INTRODUCTION

Based on the Austrian Environmental Support Act the Kommunalkredit Public Consulting GmbH since 1993 has been managing the environmental support schemes of the federal government as a contractor of the Federal Ministry of Environment. Among these environmental support schemes the Remediation of contaminated sites since 1993 up to 2012 includes a total amount of 205 remediation projects representing investments of 986 EUR million with granted support of 752 EUR million.

INITIAL SITUATION AND INDUCEMENT

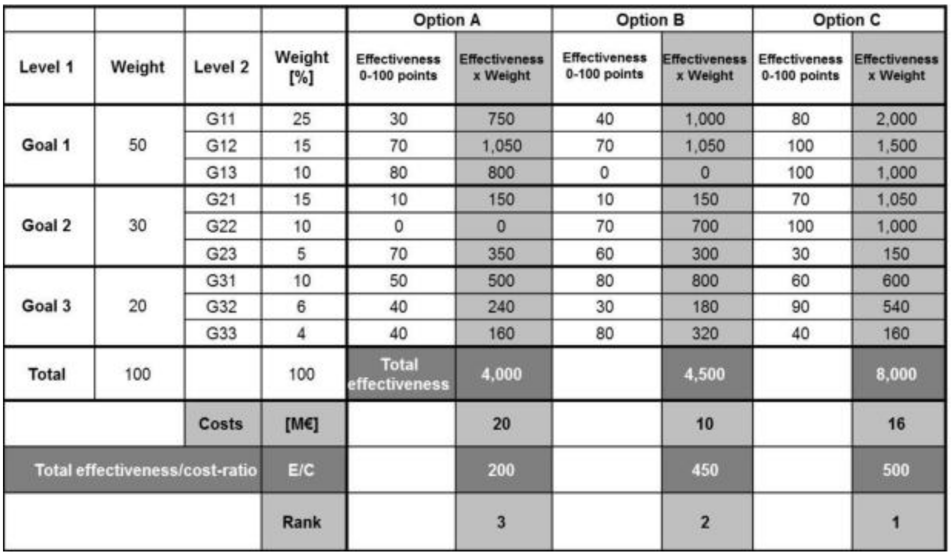
The Austrian federal funding guidelines for remediation are based on the principle of "maximum ecological effect under acceptable macroeconomic cost". According to this the ecological-economic assessment of remediation alternatives is a main precondition for Austria´s public funding. Since the criteria for these assessments have not been standardized, Austria´s Federal Ministry of Environment launched the development of an appropriate standardized assessment tool in 2010 aimed to become mandatory when requesting resources from the national Remediation Fund.

MODIFIED COST-EFFECTIVENESS-ANALYSIS (MCEA)

Starting point for proposing a standardized assessment procedure of remedial options was an extensive literature review on available assessment methods and tools carried out by the authors (Ortmann & Döberl, 2010). The methods and tools were evaluated regarding the issues suitability to the principles of sustainability and contaminated land management according to the Austrian "Mission Statement on Contaminated Site Management" (BMLFUW, ed., 2009), transparency and reliability in order to avoid „black-box-effects", flexibility regarding the adaption to specific needs and user-friendliness. A modified Cost-Effectiveness-Analysis (MCEA) was identified as the most appropriate assessment method (Ortmann & Döberl, 2010). Classical CEA are commonly used in the public sector to identify the most advantageous among different options. Ideally, it is the option combining the least costs with the highest effectiveness in fulfilling specific objectives. The result of a classical CEA is a comparison of the costs of an option with a matrix displaying the effectiveness values regarding different objectives.

The Modified Cost-Effectiveness (MCEA) was developed allowing for an aggregation of effectiveness values at different levels and to calculate a total effectiveness-cost-ratio enabling a ranking of options. Like a classical CEA, an MCEA consists of an effectiveness assessment on the one hand and an assessment of corresponding costs on the other hand.

Effectiveness assessment displays the effectiveness values of an alternative regarding different objectives (goals). Summing up the weighted values according to the objectives leads to a total effectiveness value for each alternative. The costs of an alternative are assessed in monetary terms. The relation between total effectiveness and costs provides an effectiveness/cost-ratio for each alternative allowing a ranking and comprehensible choice of the best alternative as shown in Fig. 1.



				Option A		Option B		Option C	
Level 1	Weight	Level 2	Weight [%]	Effectiveness 0-100 points	Effectiveness x Weight	Effectiveness 0-100 points	Effectiveness x Weight	Effectiveness 0-100 points	Effectiveness x Weight
Goal 1	50	G11	25	30	750	40	1,000	80	2,000
		G12	15	70	1,050	70	1,050	100	1,500
		G13	10	80	800	0	0	100	1,000
Goal 2	30	G21	15	10	150	10	150	70	1,050
		G22	10	0	0	70	700	100	1,000
		G23	5	70	350	60	300	30	150
Goal 3	20	G31	10	50	500	80	800	60	600
		G32	6	40	240	30	180	90	540
		G33	4	40	160	80	320	40	160
Total	100		100	Total effectiveness	4,000		4,500		8,000
		Costs	[M€]		20		10		16
Total effectiveness/cost-ratio			E/C		200		450		500
			Rank		3		2		1

Fig. 1. Example results of MCEA (modified after Ortmann & Döberl, 2010)

HIERARCHIC SYSTEM OF GOALS AND WEIGHTINGS

Since the application of MCEA requires objectives and goals to be defined, a hierarchic system of objectives, goals and weightings categories has been established. Representatives of Austria's relevant stakeholder groups in contaminated site management have been involved in discussing, critically reviewing and amending the proposed objectives, goals and weightings. This stakeholder-process resulted in a hierarchical system of goals consisting of 4 levels (level 1: overall objectives; level 2: goals; level 3: indicator categories and level 4: criteria), each level specifying the goals of the level(s) above. The goals of the upper levels and their weighting are derived from national laws, guidelines and other relevant international documents. These upper-level goals and their weightings remain pre-defined by the public funder. The goals of the lowermost level ("criteria") are represented by measureable (quantitatively or qualitatively) criteria and not pre-defined but to be specified by the planning engineer in accordance with the site-specific situation and with local stakeholders. This is why level 4 is not represented in the figures below.

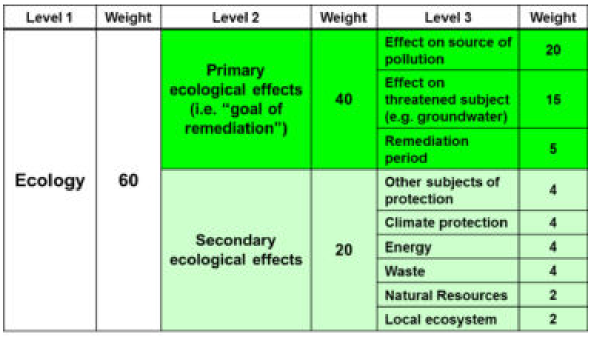
The goals of the uppermost level („overall objectives") and their weighting have been defined within the stakeholder process as follows:

- Objective 1: „Ecology" (Weight 60 %): Maximizing the ecological benefit.
- Objective 2: „Local Development" (Weight 20 %): Improving the framing conditions for local development.
- Objective 3: „Project Stability" (Weight 20 %): Improving further aspects of sustainability.

According to its importance the costs are not a part of the goal-system but integrated as a separate parameter into the algorithmus of the MCEA as described in the previous section.

Overall Objective 1 – "Ecology"

The overall objective "Ecology", i.e. "maximizing the environmental benefit" is split into the goals "primary environmental effects" and "secondary environmental effects" at level 2. Primary environmental effects, generally, are the environmental goals of remediation measures, whereas secondary environmental effects comprise accompanying side effects, which mostly are unintended. Concerning primary environmental effects, as a minimum requirement remediation options need to fulfil the remediation target, otherwise they are not suitable for an assessment. It has to be noted that the remediation target has to be defined prior to the assessment.

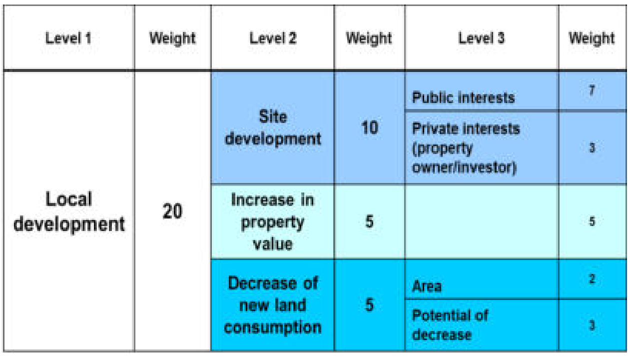


Level 1	Weight	Level 2	Weight	Level 3	Weight
Ecology	60	Primary ecological effects (i.e. "goal of remediation")	40	Effect on source of pollution	20
				Effect on threatened subject (e.g. groundwater)	15
				Remediation period	5
		Secondary ecological effects	20	Other subjects of protection	4
				Climate protection	4
				Energy	4
				Waste	4
				Natural Resources	2
				Local ecosystem	2

Fig. 2. Overall objective “Ecology” with further–level–goals and weightings

Overall Objective 2 – “Local Development”

Although the commercial reuse of (formerly) contaminated sites is not specifically deducible from legislation as a goal of contaminated site management, it is one of the main driving forces to remediate contaminated sites. Thus, it is addressed in the Austrian “Mission Statement on Contaminated Site Management” (BMLFUW, ed., 2009) by stating: “Framing conditions for reusing and integrating contaminated sites back into economic cycles shall be improved”. Besides an economic benefit for site owners or investors, a reuse of contaminated sites mostly generates a public benefit. Decreasing land consumption by reuse of brownfields and combating urban sprawl are widely recognized environmental targets, which are addressed in various policy papers at national and international level.

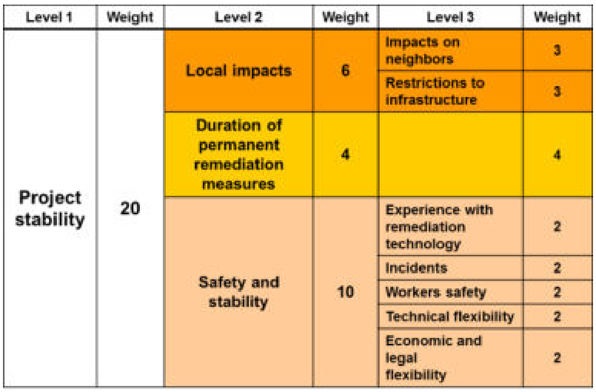


Level 1	Weight	Level 2	Weight	Level 3	Weight
Local development	20	Site development	10	Public interests	7
				Private interests (property owner/investor)	3
		Increase in property value	5		5
		Decrease of new land consumption	5	Area	2
				Potential of decrease	3

Fig. 3. Overall objective “Local Development” with further–level–goals and weightings

Objective 3 – “Project Stability”

The third objective “Project Stability” addresses aspects of sustainability, which are not covered by environmental criteria or criteria representing site development issues and costs. Hence, particularly health effects and socio-economic impacts on humans and regions as well as the stability of remediation options concerning a change in framing conditions are assessed.



Level 1	Weight	Level 2	Weight	Level 3	Weight
Project stability	20	Local impacts	6	Impacts on neighbors	3
				Restrictions to infrastructure	3
		Duration of permanent remediation measures	4		4
		Safety and stability	10	Experience with remediation technology	2
				Incidents	2
				Workers safety	2
				Technical flexibility	2
				Economic and legal flexibility	2

Fig. 4. Overall objective “Project Stability” with further–level–goals and weightings

RESULTS OF MCEA

At a first glance, the most beneficial option can be identified by the highest total effectiveness/cost-ratio among the options assessed. However, it is strongly recommended with respect to quality assurance and transparency, to complement the effectiveness/cost-ratio with cost-effectiveness matrices similar to classical CEA. Especially if the effectiveness/cost-ratio of two or more options is close to each other, cost-effectiveness matrices allow for a more complete picture on strengths and weaknesses of an option than a highly aggregated single indicator.

Dealing with uncertainties of input data is another crucial issue regarding the reliability and transparency of results. In order to evaluate the stability of results and the robustness of the ranking, it is recommended to perform sensitivity analyses by varying input data according to their uncertainties. Due to its high influence on the result and practical experiences with cost estimations, particularly changes in costs should be investigated regarding their impact on the ranking. A check of potential changes in ranking is suggested by modifying the costs ± 15%. In order to provide an appropriate basis for decision making, the IT-tool (see below) allows for a display of input data, MCEA-matrices and graphs of the results including sensitivity analyses.

APPLICATION OF MCEA INTO CONTAMINATED SITE MANAGEMENT

In order to support the application of MCEA in practice, a Microsoft-Excel-based IT-tool has been developed enabling structured data input, processing and output. A German version of the tool as well as a manual, providing more detailed information on the practical application and instructions on the hierarchic system of goals (Ortmann et al., 2011) is available for free on the website of the Kommunalkredit Public Consulting GmbH as authorized body in charge of managing the funding in contaminated site remediation. The MCEA (including manual and software-tool) was implemented in January 2012. It has to be used obligatory for studies on remediation alternatives as a part of the application for national funding.

SUMMARY AND PROSPECT

First practical experiences with the assessment tool leading to reasonable results. Nevertheless further periodic reviewing of the assessment results regarding their reliability and robustness is exspected. Furthermore, the methodology and the IT-tool seem to be accepted by the majority of practitioners, which, according to the authors' opinion, is mainly owed to the stakeholder involvement from the very beginning of the development process.

Implementing the methodology into the funding regime may be seen as a basic element for the efficient use of public and private resources in future contaminated site management in Austria.

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TOWARDS A NEW CONTAMINATED SITES ORDINANCE ESTABLISHING COMPREHENSIVE ASSESSMENT CRITERIA IN AUSTRIA

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KEYWORDS

ALSAG – Altlastensanierungsgesetz, Austrian law, ordinance, contaminated sites, prioritisation, assessment, risk based classification

ABSTRACT

By the end of 2012 a complete revision of contaminated sites legislation in Austria has been drafted. Under the revised law, which still will keep to address only historical contamination (before 1990), an ordinance shall provide criteria to assess and identify ‘significantly’ contaminated sites as well as ‘seriously’ contaminated sites. The draft ordinance addresses a typology of frequent contaminants. Tailored with respect to contaminant behaviour a comprehensive set of assessment criteria on (i) intensity (contaminant concentration), (ii) the extent (volume or area) and (iii) effect related issues (e.g. mass flows) is provided. The presentation will explore the scientific and technical background to define the proposed criteria sets and summarize major learnings and amendments of stakeholder discussions.

ENVISAGED LEGISLATIVE CHANGES

In the year 1989 the Act on the Remediation of Contaminated Sites (ALSAG 1989) was set in force in Austria. This Act was generally dedicated to provide financial resources for the remediation of contaminated sites such as landfills and industrial sites by introducing a tax on landfilling of waste. The revenue is earmarked for funding remedial projects (85 %), for identifying and investigating (potentially) contaminated sites and prioritising seriously contaminated sites (15 %). Lessons learned during more than 20 years of investigating and remediating contaminated sites in Austria as well as the on-going international discussion on risk based assessment approaches and remediation goals resulted in recognizing a need for a major revision of ALSAG.

ALSAG 2013, a complete revision of ALSAG 1989, which has the status of a legislative proposal at the moment, has the aim to identify contaminated and seriously contaminated sites. It is intended to form a basis the extent of remedial actions on seriously contaminated sites can be derived from in order to reduce and monitor risks for human health and the environment. As the “old” (but still in force) legislation, ALSAG 2013 will still be restricted to historical contamination (prior to 1990) and will not be applicable for contamination originating from agriculture and forestry, mining, radioactive substances, explosive substances and emissions in the atmosphere or in surface water.

In addition to the financial focus of ALSAG 1989, ALSAG 2013 addresses systematic identification of contaminated sites, effect and land-use related risk assessment, appropriate actions and risk minimising measures. Additionally, the criteria describing the terms “contaminated” and “seriously contaminated” sites have been defined quantitatively in an accompanying ordinance. .

ASSESSING AND CONTROLLING RISKS

The basis for risk assessment and risk control is the knowledge about intensity and extent of contamination. Furthermore it is also essential to know about the duration that the contaminant is present in the soil, air or in groundwater. As a following step a risk based assessment of contaminated and seriously contaminated sites is the basis for the classification and prioritisation.

Especially four points have to be recognised:

- Migration of gaseous and liquid pollutants (migration of landfill gas or substances in the groundwater)
- Impacts of pollutants on the soil or surface water
- Issues regarding land-use ; e.g. risks originating from flammable or suffocating gases, potential impact of contaminants for human health, increased mobilisation of contaminants
- Risks for human uptake of contaminants (to inhale, drink or eat but also to get in dermal contact) with

Risk assessments have to be performed basically on an effect-related basis taking into account land-use related issues. This applies for remedial measures as well. However, non-tolerable risks for human health or the environment have to be excluded.

GENERAL CRITERIA TO DETERMINE AND REGISTER CONTAMINATED SITES

As already mentioned in Austria each site, especially each historical site and landfill can be classified in the following 3 categories after investigation work:

- not contaminated or only minor contaminated
- contaminated
- seriously contaminated

A contaminated site is a definable area or site with a more than minor contaminated subsurface or more than minor amount of landfilled waste. At a seriously contaminated site it is necessary to take remedial actions. These can be a further investigation, monitoring with natural attenuation or monitoring with remediation work.

Tailored with respect to contaminant behaviour a comprehensive set of assessment criteria on (i) intensity (contaminant concentration), (ii) the extent (volume or area) and (iii) effect related issues (e.g. mass flows) is provided:

- Chlorinated Hydrocarbons
- Mineral oil
- Tar oil
- Metals
- Landfills with the potential of landfill gas production

In the following two chapters details about oil spills (mineral oil) and landfills with the potential of landfill gas production are described in detail. Regarding chlorinated hydrocarbons the ordinance defines criteria for the sum of CHC, tetrachloroethene, trichloroethene and vinyl chloride. Concerning tar oil the sum of polycyclic aromatic hydrocarbons, naphthalene, phenol index, sum of phenol and alkyl phenols are the important assessment values. In the case of a contaminated site with metals, not only the concentration and extent is important, but also the site specific availability for plants, animals or humans. All tables with criteria and trigger values concerning CHC, tar oil and metals are part of the new ordinance but not included in this paper.

It has to be noted that it is still necessary to make a risk assessment especially for each investigated landfill or historical contaminated site. It is not possible, even not with this new ordinance, to make general or global assessments for groups of sites or landfills.

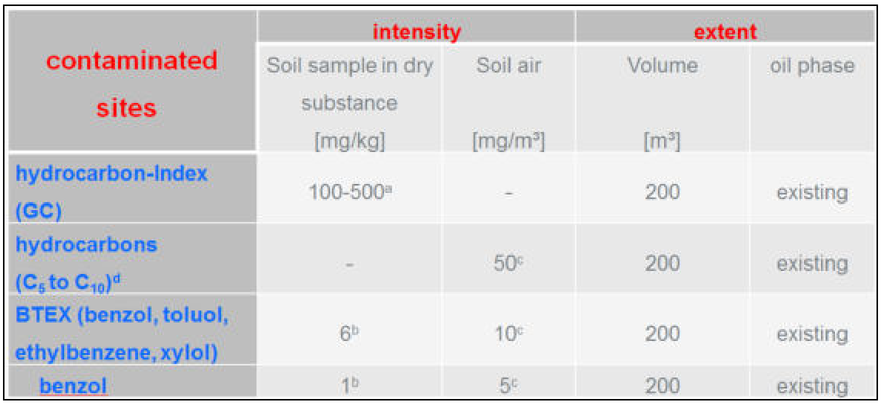
SPECIFIC CRITERIA REGARDING OIL SPILLS

In tab. 1 the criteria for sites contaminated by mineral oil are presented.

A site is "contaminated",

- if the value (tab. 1) of the contamination and the value for the contaminated volume are exceeded or
- if an oil phase exists on the groundwater table.

Tab. 1. Criteria and trigger values for contaminated sites



contaminated sites	intensity		extent	
	Soil sample in dry substance [mg/kg]	Soil air [mg/m³]	Volume [m³]	oil phase
hydrocarbon-Index (GC)	100-500[a]	-	200	existing
hydrocarbons (C_5 to C_{10})[d]	-	50[c]	200	existing
BTEX (benzol, toluol, ethylbenzene, xylol)	6[b]	10[c]	200	existing
benzol	1[b]	5[c]	200	existing

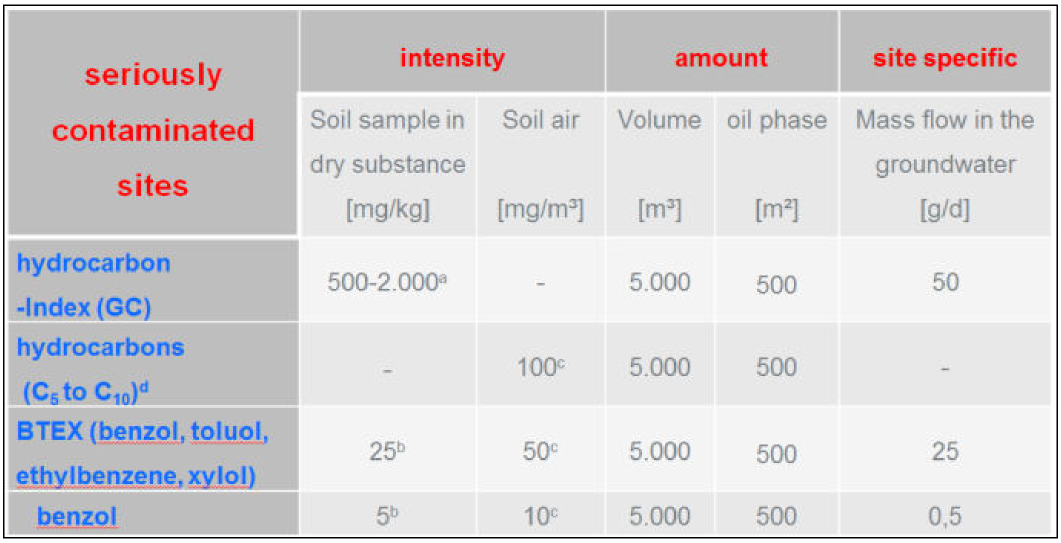
In tab. 2 the criteria and trigger values for sites seriously contaminated by mineral oil are presented.

A site is "seriously contaminated",

- if the value (tab. 2) concerning the intensity of the contamination and the value for the contaminated volume are exceeded or

- if an oil phase with an extent larger than 500 m² exists on the groundwater table or
- if the value for the mass flow in the groundwater is exceeded and the value for the contaminated site (tab. 1) is fulfilled.

Tab. 2. Criteria and trigger values for seriously contaminated sites



seriously contaminated sites	intensity		amount		site specific
	Soil sample in dry substance [mg/kg]	Soil air [mg/m^3]	Volume [m^3]	oil phase [m^2]	Mass flow in the groundwater [g/d]
hydrocarbon -Index (GC)	500-2.000[a]	-	5.000	500	50
hydrocarbons (C_5 to C_{10})[d]	-	100[c]	5.000	500	-
BTEX (benzol, toluol, ethylbenzene, xylol)	25[b]	50[c]	5.000	500	25
benzol	5[b]	10[c]	5.000	500	0,5

[a] … The values are dependent from element group specific mobilisation according to the mineral oil product. For low temperature boiling, easily mobilised hydrocarbons (< C22) a value higher than 100 mg/kg (if contaminated) respectively 500 mg/kg (if seriously contaminated), or the proportion of high boiling hydrocarbons is higher than 80 % (> C30) a value higher than 500 mg/kg (if contaminated) respectively 2.000 mg/kg (if seriously contaminated).

[b] … The values for BTEX in dry substance (soil sample) are only applicable in low permeable underground ($k_f<10^{-5}$ m/s)

[c] … The values for soil air concentration are only applicable in high permeable underground ($k_f>10^{-5}$ m/s)

[d] … The parameter includes aliphatic (n- und i-Alkane, cyclo-Alkane, Alkene) as well as aromatic hydrocarbons (C_6-C_{10}-aromates).

SPECIFIC CRITERIA REGARDING SANITARY LANDFILLS

In tab. 3 the criteria and trigger values for landfills with landfill gas production are shown.

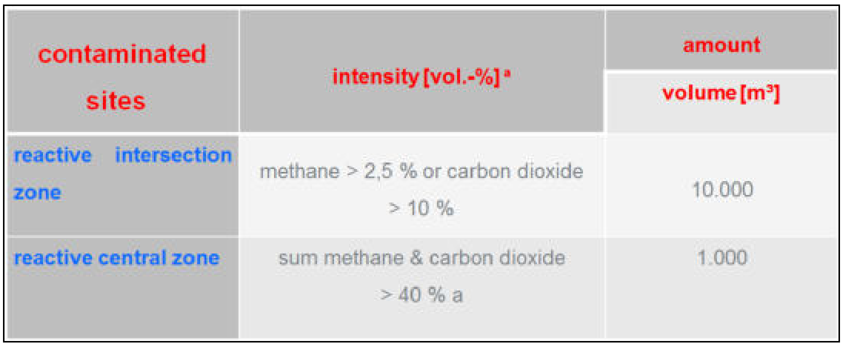
A site (landfill) is “contaminated”,

- if the values (tab. 3) of the intensity (reactive central zone or reactive intersection zone) and the values for the contaminated volume (reactive central zone or reactive intersection zone) are exceeded.

A site is “seriously contaminated”,

- if the value (tab. 4) concerning the intensity (reactive central zone or reactive intersection zone) and the value for the contaminated volume (reactive central zone or reactive intersection zone) are exceeded or
- if the value for the mass flow in the groundwater is exceeded and the value for the contaminated site (tab. 3) is fulfilled or
- if a hazard from landfill gas exists and the criteria (tab. 3) of the contaminated site (tab. 3) are exceeded.

Tab. 3. Criteria and trigger values for contaminated sites

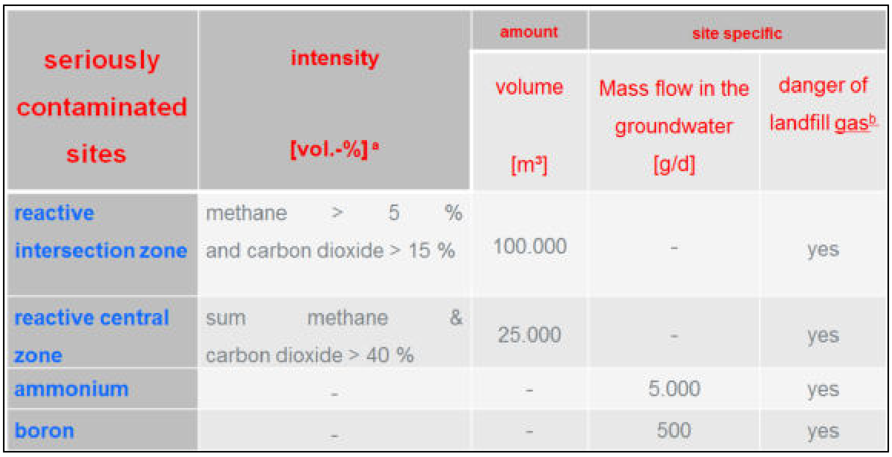


contaminated sites	intensity [vol.-%] [a]	amount
		volume [m³]
reactive intersection zone	methane > 2,5 % or carbon dioxide > 10 %	10.000
reactive central zone	sum methane & carbon dioxide > 40 % a	1.000

By assessing the reactive potential of a landfill or by checking the plausibility of the landfill gas concentrations, further criteria have to be considered beside the criteria of Tab. 3 and 4:

- History of the landfilled area
- Type, manner, structure and time of construction of the surface covering
- The proportion of the water and dry substance in the landfill
- Distance between groundwater table and the bottom of the landfill
- Organoleptic analyses of the deposit (soil sample)
- TOC in the soil analysis
- Water amount of the soil samples

Tab. 4. Criteria and trigger values for seriously contaminated sites



seriously contaminated sites	intensity [vol.-%] [a]	amount	site specific	
		volume [m³]	Mass flow in the groundwater [g/d]	danger of landfill gas [b]
reactive intersection zone	methane > 5 % and carbon dioxide > 15 %	100.000	-	yes
reactive central zone	sum methane & carbon dioxide > 40 %	25.000	-	yes
ammonium	-	-	5.000	yes
boron	-	-	500	yes

[a] …investigation of landfill gas according to the Austrian Norm ÖNORM S 2090

[b] …By a site specific assessment of a potential danger from landfill gas originating from gas migration in the underground the following points are necessary to address:

- Type (e.g. cellar), local situation and the utilisation of the object (building or installations in the underground e.g. inspection pit for rainwater)
- Location of the landfill gas control points to potentially concerned objects
- Results of landfill close by a landfill

CONCLUSIONS AND THE WAY ONWARDS

Besides in-depth discussions regarding the criteria to characterise the intensity of contamination, in particular discussions on trigger values to benchmark the extent of contamination proofed more challenging and controversial. As long as there are still unsolved questions whether serious contamination and environmental or human health risks are linked directly. However, it is expected that discussions will be finalised by 2013 and the revised legislation will be in force by 2015.

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A STRATEGY TO DEFINE LEGISLATION ON SOIL CONTAMINATION – THE PORTUGUESE EXAMPLE

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KEYWORDS
Legislation, contaminated soil, potentially contaminated soil, risk assessment, human health, ecosystem, technical guidelines

ABSTRACT

The need to develop specific legislation on contaminated soil and a set of technical guidelines designed to support the legislation, led Portugal to conduct a benchmark study on legislation of some European and North American countries. In the absence of data that would allow to derive our own reference values, we opted for the use of the reference values for Ontario complemented with the values of Spanish Standards for heavy metals. The maximum probability of acceptable risk to human health values were set at $1x10^{-5}$ to carcinogens contaminants and at 1 for non-cancerous contaminants. Acceptable risk for Ecosystems was set at 1 and was created an exclusion criterion, prior to risk assessment, based on the model used in Washington. The soil evaluation methodology has three distinct phases and there will be three types of land use. Legislation will also set the criteria to outline responsibilities in the management and remediation of contaminated soils.

The purpose of this assignment is to explain the methodology used by Portugal in the creation of legislation on contaminated soils. It was a strategy based on the analysis of what already exists in other countries, adapting the measures that best suited Portugal’s needs, interests and goals.

The Portuguese Environment Agency, I. P. (APA, IP) is a public institution within the Ministry of Agriculture, Sea, Environment and Spatial Planning (MAMAOT), under the direct supervision of its Minister or one Secretary of State.

Its mission is to propose, develop and monitor the environmental and sustainable development policies and manage and coordinate its integration with other sectorial policies, in collaboration with other entities, public and private.

Its assignments are to propose, develop and monitor the implementation of environmental policies in a vast range of environmental issues, particularly in combating climate change, waste management (National Waste Authority) and water resources (National Water Authority), the protection of ozone layer and air quality, restoration and enhancement of soil and other contaminated sites, Integrated Pollution Prevention and Control (IPPC Directive), prevention and control of noise, control of major-accident hazards involving dangerous substances, prevention and remedying of environmental damage Directive, safety of environment and populations, eco-labeling, the green purchasing, systems of voluntary environmental management, as well as the environmental impact assessment and environmental assessment of plans and programs.

It has legal powers to emit permits on certain activities, to create technical guidelines and standardize procedures in specific environmental matters and to connect the Portuguese Government with various international bodies related to the environmental issues of its scope.

It was in this context of assignments that the APA, IP decided to proceed with the preparation of a legal framework on contaminated soils. Four factors were crucial:

- The elaboration of the "Strategy for Contaminated Soils, 2011-2016", listing a series of actions to be developed and establishing deadlines for its implementation. This strategy is supported on the principles of prevention and reparation, so as to safeguard human health and the Environment, allowing its sustainable use by humans. The principle of prevention is ensured through the development and implementation of a set of legal, technical, economical and administrative instruments, whilst the corrective aspect focus on developing an action plan to be put in practice on places identified as problematic and of high priority;
- The blocking of the proposed European directive framework on soil imposed by a minority of the Member States in the Council 'Environment' of March 2010, citing reasons of subsidiarity, excessive costs and administrative burdens. Portugal was awaiting the approval of that directive to have a working basis on which to develop their own law on contaminated soil;

- The increasing number of requests for information on how to determine soil quality, particularly by foreign companies seeking to invest in Portugal and by companies seeking to dismantle partly or whole industrial units. Due to the lack of specific norms, the Portuguese Authorities recommends the use of the Ontario Standards (Soil, Groundwater and Sediment Standards for Use Under Part XV.1 of the Environmental Protection Act, July 27, 2009) or the Dutch Standards (Target Values and Intervention Values for Soil Remediation);
- The legal aspects of managing contaminated soils are currently outlined, in a very briefly manner, under the legislation on waste (Law Decree No. 178/2006 of 5 September, that transposed the Directive 2008/98/EC of the European Parliament and of the Council of 19 November, as amended by the Law Decree No. 73/2011 of 17 June), through the obligation of submitting the decontamination of soils prior to licensing.

The creation of the guidelines that will support the upcoming legislation on contaminated soil was initiated in late 2011, with the hiring of a technical consultant to:
- Develop an action model for contaminated soils, designed to ensure the sustainable use of soil through protection of its quality;
- Purpose a methodology to establish the degree of contamination and define the parameters of management or remediation of contaminated sites;
- Elaborate the documents and technical standards and guidelines, designed to support the future national legislation on contaminated soils in an understandable manner to the public in general.

The objective is to produce the following documents:
- Legal and Methodological Benchmark;
- Methodological Guide to the Declaration of Soil Quality;
- Guide for Risk Analysis;
- Preliminary Report of the State of Soil with a computer application;
- 5 Technical Guides: Sampling Plan for Contaminated Soils and Groundwater, Sample Collection of Contaminated Soils, Chemical Analysis for Contaminated Soils, Best Available Techniques for Soil Decontamination and Guide for the Prevention of Soil Contamination.

The process began with *Legal and Methodological Benchmark* report which made the comparative analysis and critical discussion of the laws and methods existing in some European countries (Austria, Germany, Netherlands, Spain, United Kingdom) and North American countries (states of Texas and Washington in the USA and Ontario Province in Canada), paying special attention to aspects relating to:
- Site investigation;
- Risk assessment;
- Management and remediation , including orphan contaminated sites and voluntary remediation procedures;

with the goal of developing a Portuguese legal framework based on the experience and best practices of each country. The use of processes and methodologies already applied and verified in other countries provide some assurances of their efficiency and reliability.

As a result of the findings of this benchmark report, a *Methodological Guide for Soil Quality Declaration* was elaborated, setting the guidelines and steps that must be followed during the investigation of a potential contaminated soil or site in mainland Portugal. Among the most relevant aspects defined in this document we stand out:
- Definition of the universe of sectors, activities and other possible menacing situations: industrial activities (based on thresholds of production and/or storage of hazardous substances – IPPC Directive, prevention and remedying of environmental damage Directive, control of major-accident hazards involving dangerous substances Directive), other activities related to storage and use of hazardous substances or hydrocarbons and their derivatives (based on thresholds of storage capacity) units for treating industrial and oil refining wastewater, waste management (hazardous waste recovery and recycling, urban, organic or hazardous wastes disposal, remediation of contaminated soils), transport activities of goods, materials and products containing substances or mixtures classified as hazardous or dangerous;
- Definition of a procedure of soil quality investigation made up of three phases, as most European models: preliminary investigation, exploratory investigation and detailed investigation;
- Definition of reference values: in the absence of specific studies on the national lithology background characterization, turned out to be necessary, for now, the use of values already derived and defined. Being historically recommended and implemented in processes of investigation of contaminated soil in Portugal, meaning existing familiarity with their use, and due to its quite conservative nature, simultaneously ensuring that any potential risk is identified in this sieve, the option fell on the reference values defined in the Ontario Standards.

For heavy metals, the initial approach was to adopt the reference values of Ontario Standards, which, when possible, will be corrected with background lithological values available for some regions of Spain (Galicia and Madrid) since those two regions have geological affinity to certain areas of Portugal. Until the adoption of national derived lithological background values, the responsible for the soil investigation may choose to use the defined reference values or its own local lithological background values. In this case, these values together with the sampling and collection plan are subject to prior approval of the Competent Authority;

- Definition of three classes of land use: agricultural use (includes others uses), residential use (includes green areas and recreational uses), industrial (includes commercial use);
- Issuing of a Declaration of Soil Quality: document emitted by the Competent Authority which will include the type of authorized use of soil, data on pollutant levels, remediation technique(s) used and obtained results.

According to this methodology, the preliminary investigation will define the situations in which soil contamination might have occurred.

In such cases, it becomes necessary to go forward an exploratory investigation that includes field analysis on expected contaminants, for later comparison of the obtained values against reference values.

If they are not surpassed, the process finishes. If they are exceeded, it is necessary to move on to the stage of detailed investigation, which includes analysis of risk assessment to human health and/or to ecosystems.

To support the fulfillment of this risk assessment it was provided a *Guide for Risk Assessment*, designed to define the methodology to quantify the risk to human health and ecosystems, outlining the acceptable probability of risk:

- Quantification of an acceptable probability of risk to human health: the maximum acceptable probability of risk was set on $1x10^{-5}$ for carcinogens pollutants and at 1 for non-cancerous pollutants. These values ensure an acceptable risk of the exposed receptors and are in accordance with most European countries;
- Quantification of an acceptable probability of risk to ecosystems: the value 1 was defined as the maximum probability of acceptable risk. Due to the technical complexity of this type of analysis, an exclusion criterion was defined prior to risk analysis, based on the Washington Regulation. If none of the following assumptions (contamination in depth, presence of pavement or other physical barrier to prevent contact with animals or plants, low sensitivity ecological environment) is fulfilled then it will be necessary to make a simplified risk assessment. If at least one of the assumptions is satisfied but there is still the possibility of discharge of contaminants in surface waters it will be also necessary to make a simplified risk assessment. If at least one of the assumptions is satisfied but there is no possibility of discharge of contaminants in surface waters then it is exempted of risk assessment. In the event of a potential risk to one or more organisms in an ecosystem, or in those cases where it is not possible to determine the effects of a contaminant on an organism through a simplified risk assessment, it will be necessary to undertake a detailed risk assessment.

The risk assessment to human health and ecosystems can be performed by any of the methodology used internationally (RBCA) and using international databases (IRIS HEAST, CalEPA, WHO, IUCLID, RIVM).

Directly linked to these guidelines is the *Preliminary Report of Soil Condition*. This is an exhaustive report of the current and past situation of the potentially polluting activity and it is the first step (preliminary investigation) of soil contamination characterization. Through a technical analysis associated to a computer application, the provided information is analyzed allowing to quantify the contamination potential resulting from the aforementioned activity. If the value obtained exceeds 50 points on a 100 point scale, one can consider to be enough traces of possible contamination and should thereof be performed an exploratory investigation.

The 4 technical guidelines *Sampling Plan of Contaminated Soils and Groundwater*, *Sample Collection of Contaminated Soils*, *Chemical Analyses for Contaminated Soils* and *Best Available Decontamination Techniques* are intended to acquaint a set of information to assist the responsible for the decontamination of a site to understand the complexity of the task at hand and provide guidance in the contracting process of the company with the best and most suitable technical options.

In turn, the *Guide of Prevention Measures of Soil Contamination* offers a set of tips and techniques to prevent soil contamination as a result of accidents, negligent practices or simple lack of technical knowledge.

As stated, these technical documents will be supported by specific legislation. Among the various legal and technical matters enclosed by that, we highlight the following considerations:

- The definition of the procedure for licensing, monitoring and follow up of projects of investigation and decontamination of soils and sites;

- The definition of the situations of mandatory soil condition characterization upon transfer of ownership and/or land use change;
- The registration of the Declaration of Soil Quality on the Land Register to ensure that before or upon transfer of ownership the buyer can acknowledge of the soil condition and of the responsibilities thereof;
- The creation of a national database of potentially contaminated and contaminated sites available to the public in general;
- The penalties for soil contamination and breach of the legal obligation to manage or remediate contaminated soil.

In conclusion, it is not easy to create legislation on a subject as complex as soil remediation, as it is closely linked to their potential risk to human health and ecosystems. It is however possible, based on methodologies and procedures that are under use in others countries with proved effectiveness, adapt it to our particular needs and create a national model. The absence of lithological and public health studies that would allow deriving own reference values should not be seen as an obstacle to a country in developing its own legislation on contaminated soils and risk assessment. While it has not enough data permitting to derive its own reference values, it is possibly to use, in a temporarily way, values already used in other countries.

It should not be forgotten that the countries which today have complex legislation also started in a simple manner. The increase of knowledge and experience that will be accumulated over time as a result of legislation enforcement will in time be used to improve it.

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CONTAMINATED SITES INVENTORY PROJECT IN THE CZECH REPUBLIC - METHODOLOGY OUTLINES

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KEYWORDS
Contaminated sites, inventory, methodology, old environmental burdens, database

ABSTRACT

Existing Contaminated Sites Database System (SEKM) is an incremental database and represents a useable source of information about the contamination of soils and rock formations. However it doesn't cover all identifiable contaminated and potentially contaminated sites in the Czech Republic. Therefore, the Ministry of the Environment assigned the task of creating conditions for modernizing the database and to perform an inventory based on a surface survey, i.e. obtaining the fullest possible overview of contaminated sites throughout the state's territory. The first stage of the National Inventory of Contaminated Sites (NIKM) was designed as a project and co-financed by the Operational Programme for the Environment, ending in 2013. This preparatory stage of the project resulted in an approved methodology of the inventory. Among the results is a draft of the executive stage of the project, detailed manuals and the database NIKM as a part of the sustainable information system of NIKM. Starting of the second stage has been postponed. A complex methodology of inventarization has now been edited for publication. On the basis of obtained data, a process of nationwide inventory including the timing and financial demands of the second NIKM stage (2013-2015) was proposed. The creation of a sustainable information system on contaminated sites is also a part of the solution.

Framework for the inventory - methodological documents of the Ministry of the Environment (MoE)

The MoE's Environmental Risks and Environmental Damages Department's responsibility covers the issues of the remediation of contaminated sites, old environmental damage and other activities related to the issue. An integral part of the Department's competency is the running of the publicly available database system - the registry of contaminated sites. Since 2005 it was in the form of the Contaminated Sites Database System – "Systém evidence kontaminovaných míst" (SEKM) – www.sekm.cz. Priority evaluation and a risk profile of each contaminated site is also included in SEKM. The set of the MoE's methodological documents comprises Methodological Guidances (7 documents), Methodological Handbooks (6 documents) and other Guidelines and Guidances (3 documents). In relation to the issue of the contaminated sites inventory the most important is the Methodological Guidance of the Ministry of Environment for the filling in the SEKM database incl. a priority evaluation (2011). In 2008 the Ministry of the Environment decided, in connection with the task from the State Environmental Policy, to create conditions for modernizing the database and to perform an inventory based on a surface survey, with the aim to obtain the fullest possible overview of contaminated sites throughout the state's territory. Based on the call from the Czech Operational Programme Environment (EU Cohesion Fund), a project proposal of the National Contaminated Sites Inventory (NIKM) was prepared by CENIA. After being approved in 2009, the NIKM project was run by a project team composed by CENIA and several suppliers selected from an open public tender process.

Project Status - National Contaminated Sites Inventory (NIKM)

The first stage of the NIKM project was to be finished by the first half of 2013. Its basic goals were:

- elaboration of methodology and tools for territorial inventory planned as the second stage;
- piloting and testing of developed methodology and tools including their modification according to experience obtaind in pilot areas;
- collection and unification of existing data sources containing information on contaminated sites from the state territory (needed as an input for the 2nd stage of the inventory);
- to prepare a draft of the executive stage of the project.

The first stage of the NIKM project [1] [2] was performed in the period 2009 - 2013 as a project of the Operational Programme Environment 2007-2013, Priority axe 4 - The Improvement of Waste Management and the Rehabilitation of Old Environmental Burdens, the area of intervention 4.2. - The Rehabilitation of Old Environmental Burdens ". Individual partial outcomes and final project outcomes finished in autumn 2012 (for published results see e.g. [3] [4] [5] [6]) were externally reviewed and subjected to relevant tests (software, programme solutions and application tool tests) [7]. Descriptions of the solutions hereinafter referred to are based on the partial outputs of the project, especially [8] [9] [10] [11] [12]. Detailed information from the project is publicly disclosed on the project web site: http://www1.cenia.cz/www/projekt/nikm.

Application solutions - inventory tools

In the frame of the NIKM project, an information system for ensuring contaminated site registration is under development. The registr - database will contain the contaminated sites already registered in the existing system of SEKM and the contaminated sites newly registered during inventory. An application support (application platform – see Fig. 1) for inventory works is composed by:

- On-line application **NIKM Editor** – client environment available through a web browser. It allows record management in the central data warehouse, data editing, inserting of measurements and other findings.
- Off-line application **NIKM Client** – allowing field data collection.
- **Web portal NIKM** – for publishing data on contaminated sites for the general public and public administration.
- **Central Data Warehouse** built up on the Oracle 11g platform. Client applications are built up on a JSF basis. The grafic component ensuring the GIS Client functionality is based on OpenGIS standards and uses Javascript, AJAX technologies.

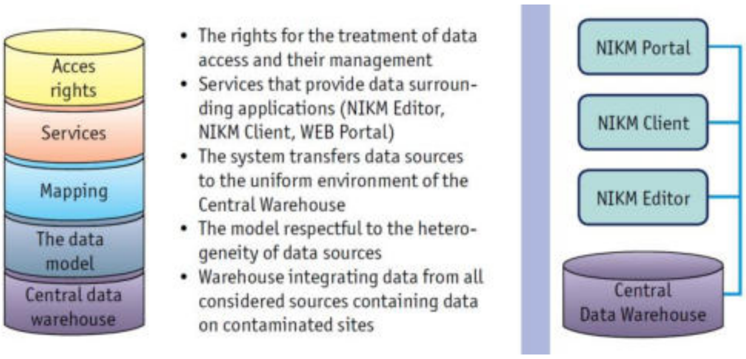

Fig. 1. Technological scheme of application platform

NIKM Editor is a centralized web application – a tool for collecting, processing and management of all data on localities stored in the NIKM central data warehouse. The application ensures data editing, background documents evaluation and data preparation for field examination (generation of the list of localities from the defined area, acquisition and completion of data from external sources), receiving modified data from the field application (NIKM Client) and a subsequent evaluation of necessary corrective measures being a priority.

Records of potencial contaminated sites and contaminated sites and of subordinated entities (drill holes, constructions, remmediations, and partial areas of localities), are all stored in the central warehouse, form a data background for the application.

The main output from the application is a printed set of data on locality in the form of a so-called - Summary form. Its content and structure are defined by the Methodological Guidance of the Ministry of Environment (2011) [13]. For the purpose of data completation there are available editable forms containing data on locality, and map sectors used for special localization and for the display and analysis of maps. An inventory expert can add any map sources in the form of a WMS service or local GIS data in various formats. The system architecture includes the map server - Geoserver, which enables an export of GIS data in the dform of WMS and WFS services.

An important tool for the on-line application is the so called pairing module that provides a search and pairing of duplicate localities. Possible conflicts during parallel editing of localities are dealt with through marking localities with a lock for expert editing in the on-line application and in the off-line field application. The import function allows data import to a central data warehouse in a standardized format. An administration sectin is used to manage the data content, including access rights. The on-line application is available only to registered professional staff via a web browser. Among the supported web browsers included are MS Internet Explorer version 7 or higher and Mozilla Firefox version 3 or higher.

NIKM Client is a tool for off-line data acquisition - for collection of data on contaminated sites in-situ and ex-situ. It allows to:

- downloading the prepared data for verification, from a central warehouse of NIKM to an off-line database;

- edit data on localities, based on information collected in field investigation and interviews with the parties concerned, or to create a new locality record in the case of a new clue or contamination discovery. It also ensures the adding of document and photo attachments, text records or voice memo records and also data exports;
- displays the locality in a map and to spatial definition – navigation to the site, site bordering manually or using GPS and displaying map data;
- upload modified data about the locality, including newly-discovered, to the central NIKM warehouse.

The input level is a list of localities. It offers an overview of localities from a defined territory. There is a selection function and function for sorting records.

The second level is detailed locality information displayed through locality form divided into bookmarks: Characteristics of locality, Conflicts and threats to the environment, Contamination and remedial measures, and Attachments. In this form, the inventory expert can edit data, add and remove attachments, write text records or record voice memos, export data to a spreadsheet etc. The range of recorded data in the form is given by print set on data to the locality in the format of Summary form, a definition of which is given by the methodological guidelines of the MoE [13].

The last level is a mapping support for working with locality spatial data. It is formed by mapping the project containing the base layers and a layer of locality, and then by instruments providing needed functionality. The basis is a tool for editing the currently selected locality manually or using GPS. There are also tools for map control (the zoom function), GPS navigation on the selected location, calculating the coordinates of centroid or the area of the site, geodata export and map's print. Of course there is a transformation of the coordinates between projections. For saving spatial component of the locality, a layer of the type GeometryCollection was chosen, so it can be located using point, line or polygon. Map project also contains, besides geodata of the locality and its objects, also underlying layers helping in better orientation in space and precise localization. Because of the need to work off-line it is not possible to form these layers using WMS services. It is necessary to have them physically in the field. Raster documents that are stored in a predefined file-directory structure were selected. The map project loads them with the use of RasterCatalogue, ensuring their quick and easy display.

Web Portal

The website prepared for the 2nd stage of the project NIKM is designed as a professionally profiled portal - a gateway to information on contaminated sites and for work with them. The portal itself provides a number of services, the most important is the service that enables you to search the localities of contaminated sites. Through this service an access for state administration and the public to individual localities is provided. Information on the contamination and handling with the locality itself are available in the form of displaing more detailed information as well as a standardized output. The portal gateway is represented by a links catalog to services or external sources. The important parts of the portal are the tools integrating mapping services of the national geoportal with mapping services of the NIKM central warehouse. This enables the user to access not only data on the contaminated site, but also its location and display it on the map. Technologically, the portal is based on the environment and services built over WordPress (open source), where the support of data, mapping and search services was implemented.

Input content of the central data warehouse

The core of the structured and distributing data storage, ensuring through application editing, storing and managing data on contaminated sites and potencionally contaminated sites is the central data warehouse. At the start of the second stage of NIKM, its input content will be available to inventory teams. During the inventory process, all records of this initial fill will be examined, updated and evaluated or excluded as irrelevant or as a duplicate of other sites.

The input fill was prepared via the transformation and merging of partial data sources from the Czech Republic's territory. In the data warehouse there are now concentrated partial data sources that were succesfully identified and taken from their owners / operators. It represents the input source of existing information on the KM for 2nd NIKM stage. During the inventory process it will be completed with records of newly discovered KM.

The data on contaminated sites and potencionally contaminated sites originated from transformed partial data sources and are now in the central warehouse stored in a unoform format, while maintaining access to the records in their original form. The record includes information, from which the partial source of the record has come from. The result of the transformation of other data sources outside of SEKM (which will be in the 2nd stage of the inventory subjected to verification, updating, evaluation of priorities and registration) are 63,942 sites transformed from partial data sources, of which 49,809 sites resulted after merging and automatic duplicates being removed.

An important set of transformed data sources are the partial data sources REZZO (air monitoring data), ISOH (waste monitoring data), IRZ (Integrated Pollution Register) and DIAMO (mine water discharges) that, based on experience from pilot verification work of the inventory, are not relevant. These partial sources contain a total of 31,925 localities not listed elsewhere already. However, this is information that is useful for the inventory process indirectly - as the primary information is, that in a certain village there are currently certain types of production or other activities, to which could be behind the emergence of contamination in the past. In the remaining set of sites relevant to NIKM there are 17,884 localities. Even in this data set there can be expected over an estimated three thousand duplicates. A large part of sites are just in the UAP (Planning analytical materials) and at least half of the sites without coordinates are candidates for being removed as duplicates. Removal of these duplicates will be done in the input field verification of the central data warehouse.

Project Methodology

Methodology for the inventory is in the summary contained in the NIKM 2nd stage project (especially in the chapters: Inventory methodology, Organization and Management of inventory) [11]. From a formal point of view, it is a set of NIKM methodological materials that define the obligatory process of the proper inventory [9]. These are primarily documents "Inventory Methodology" (about 60 pages of A4 format), "Organization and management of the inventory" (about 120 pages) and "Manual for inventory" (about 70 pages).

Methodological materials are designed to hit on the needed completeness all of the inventory process (see fig. 2 and fig 3), and to enable a comprehensive idea of the continuity and sequence of phases and activities carried out within them and the links among them.

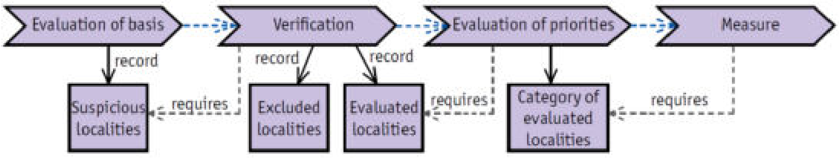

Fig. 2. Flow Chart Diagram – processes and outcomes from the inventory

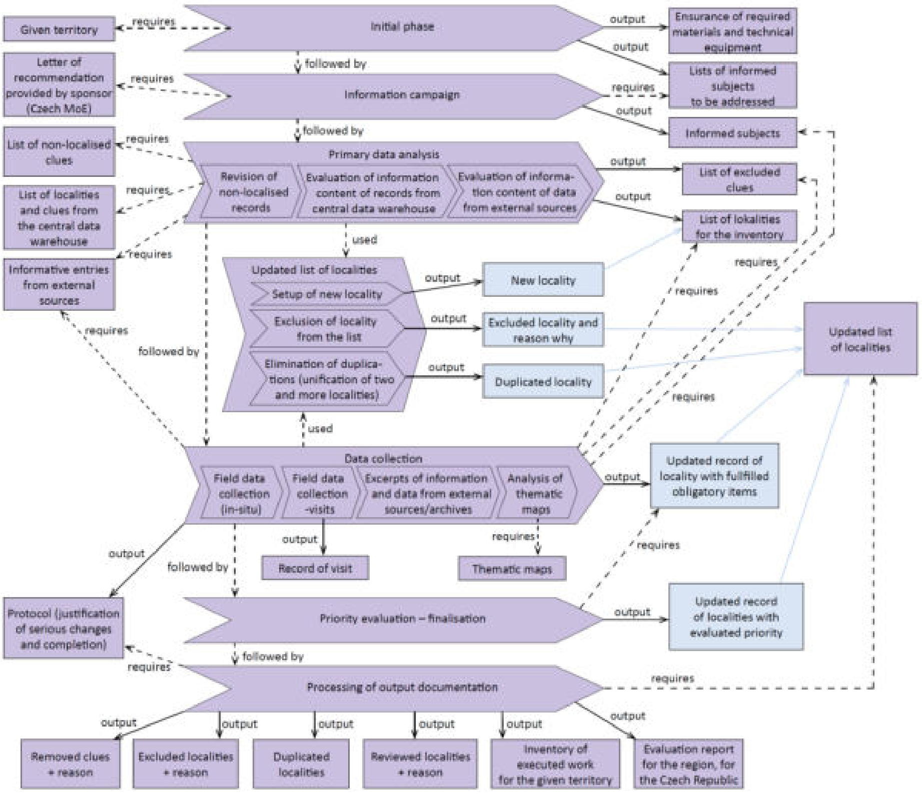

Fig. 3. Diagram of Inventory Methodology

While the document "Inventory Methodology" defines the basic conceptual principles of the inventory, the document "Manual for inventory" specifies in detail the procedures (step by step descriptions and instructions for execution) of individual activities. The document "Organization and management of the inventory" then elaborates in detail the organization and management process. The chart showing the relationships among documents in the core methodological set of the 2nd stage of the NIKM project is shown in fig. 4.

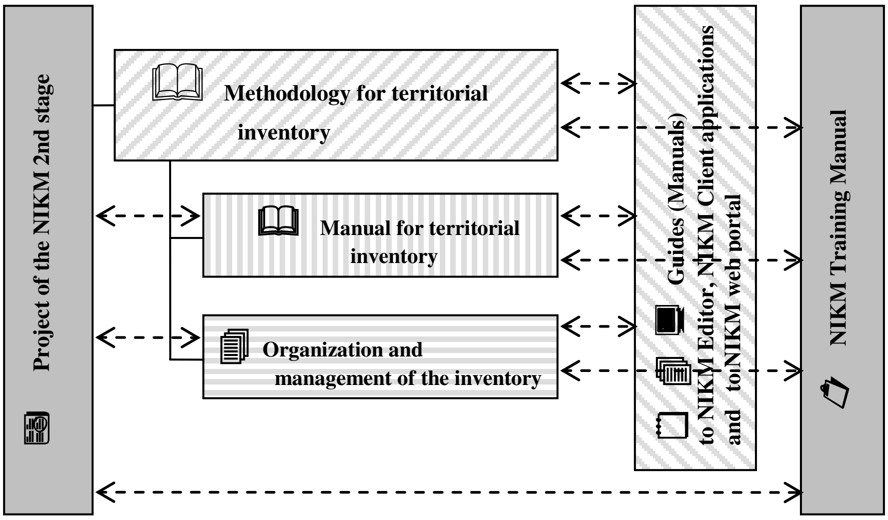

Fig. 4. Relationships among the documents composing a set of NIKM basic methodological documents

The Teritorial inventory of contaminated sites includes the executive stages “Information campaign“, “Primary data analysis“, “Data collection“ and “Priority evaluation“ (see fig. 5).

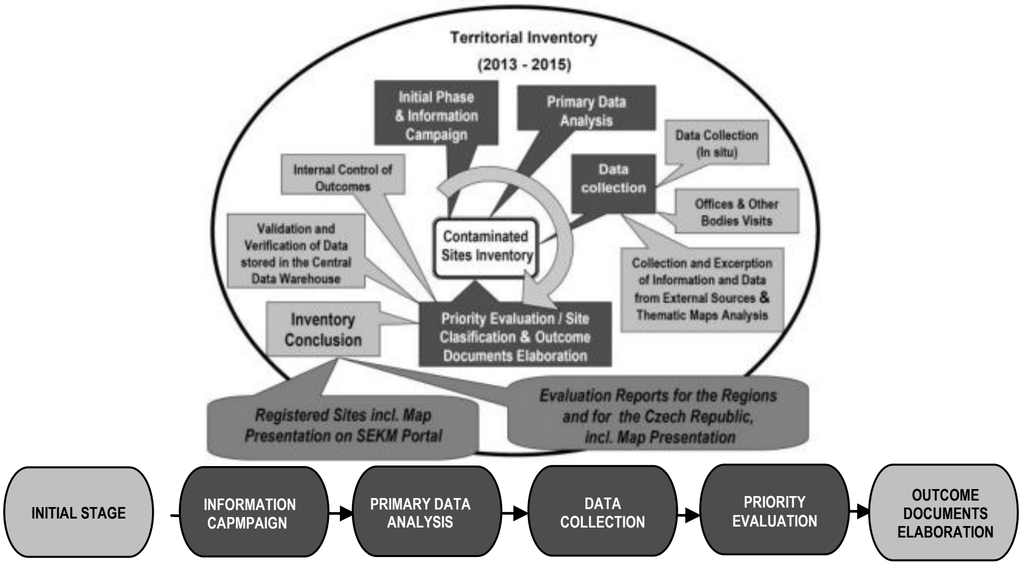

Fig. 5. Methodological fases and outcomes from the Territorial Inventory of Contaminated sites

Organization and management of the project

Implementation of the project (2nd stage) is limited by the availability of funding from the Operational programme Environment of the current programming period, ie by 2015, and by the technical and organizational aspects - by the need to manage the territorial inventory for the entire country in a maximum of two complete field seasons in the period 2013-2015. During the years 2013-2014 there should be a preparatory stage conducted, including the launch of a public tender for the supply of the inventory works, raster data and supervision. CENIA’s work includes the creation of raster data - remote sensing, merging the database of the 1st NIKM stage with the existing databases for contaminated sites (called SEKM2 in the form available at www.sekm.cz) into a single database. This will be used not only for the inventory process but simultaneously for the recording of new entries from other bodies performing investigative a remediation projects, based on the obligations under the current legislation.

Support inventory methods of remote sensing

The created raster data platform provides geographic support for the project. Prepared methodology was successfully verified in 3 pilot regions (each of them 50x50 km) representing nearly 10 % of the territory of the Czech Republic. Developed and tested methodology of identification clues for potential contaminated sites is based on the use of multispectral satellite images analysis and on the interpretation of orthophotos (current orthofotomap and orthophotomap created from historical images of the first nationwide aerial photography from the 50´s) [4]. Created orthophotomaps are placed on http://kontaminace.cenia.cz (Contaminated sites), which is already available for public viewing.

Verification activities in the 1st NIKM stage brought a lot of qualitative and quantitative knowledge about the nature of newly recorded sites, allowing for their classification into established categories of priority. Using raster data analysis, 6 571 clues of potencial contaminated sites were identified within the pilot regions. From their field examination, this resulted in less than 10 % of them being finally considered as a real potencial contaminated site or contaminated site. Examination of remote sensing clues served as the backbone of the field work's routing.

In the 2nd stage of NIKM, a specialized professional team will perform an analysis of the raster platform for the whole country. Obtained clues will be gradually sent in batches to the central data warehouse, where they will be available for inventory teams. In-situ verification of all the clues from remote sensing will be part of the field phase of the inventory.

Collecting and indicating environmental contamination

Part of the collection of information from the public in the project phase "Information campaign" will be an assembly of indications or clues of possible contamination through historical map application "Contaminated sites". Each user of this map application is already able to announce suspected localities (indication of unknown environmental contamination, eg old illegal landfills).

Discussion on the use of the methodology for other purposes

Independently of the primary purpose of the prepared methodology (i.e. for the implementation stage of the NIKM project), the question of "using it for other purposes" is frequently raised. In the case when the nationwide inventory is not launched it can be used for territorially smaller inventory projects, e.g. for regions (the Czech Republic is devided into 14 regions). There are only two pre-conditions. The first is the merging of the database warehouses of NIKM (containing transformed data sources) and SEKM2 (currenly a running system). This needs a moderate project activity to bridge several incompatibities (approx. a 6 month long project task). The second is the availability of financing (EU Funds?). The methodology can be used also for other activities – e.g for a transboundary comparison study of inventory systems in neighboring regions, or on a specialized inventory focused on selected types of contamination.

Conclusions

In 2013 the first (preparatory) stage of NIKM will be finishing, having been handled by CENIA since 2009. From 2013 it should be followed by the second (implementation) stage. In the 1st stage the project team created and verified methodology for the nationwide inventory. The project included the extraction and consolidation of the existing information on contaminated sites, involvement of remote sensing in identifying potential contaminated sites, design of inventory tools and practices and the developmet of the knowledge base for the nationwide inventory. The methodology was successfully verified in 9 % of the territory of the Czech Republic. On the basis of the methodology a procedure for the nationwide inventory, including timechedule and financial costs, was drafted.

The objective of 2nd stage is the identification, registration and basic assessment of the largest possible ammount of contaminated sites, updating information on all known locations and the creation of a sustainable information system on contaminated sites throughout the Czech Republic.

We expect that future use of the performed inventory ensures or substantially contributes to: reducing the contamination burden on the environment; more effective spatial planning; access to current information about contamination to the general public; increase the legal certainty of owners or potential owners about the status of land from the point of view of contamination; recording and evaluating groundwater contamination and the balancing of the contamination load according to the requirements of the relevant European Directives; compliance with the requirements and principles of the prospective EU Directive on soil protection; promotion of the state administration in the field of environmental damage; and, the promotion and involvement of public administration on the contamitated sites issue within the whole process (from the inventory to remmediation).

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INVENTORY OF CONTAMINATED SITES IN SERBIA

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KEYWORDS
Inventory, contaminated sites, municipal waste disposal sites, industrial sites, legal framework

ABSTRACT

Since 2005 Serbian Environmental Protection Agency started creation of National Inventory of contaminated sites. In the territory of the Republic of Serbia 338 potential contaminated and contaminated sites have been identified (Fig. 1). From the analysis of contaminated sites management data, it can be concluded that preliminary studies on all identified contaminated sites up to 2012 have been carried out, while main site investigations have been completed on a lesser number of sites. On average about 0.41 Potentially Contaminated Sites are estimated to exist per 10.000 inhabitants.

The greatest number of registered sources of localized soil pollutions is related to municipal waste disposal (39.9%), oil extraction and production (28%) and industrial and commercial activities (10.8%).

The database of potential contaminated localities within the industry was updated in 2011. There were 189 potential contaminated industrial localities on the territory of Serbia. The greatest part of the identified polluted soil localities within the industry belongs to the oil industry (51%), followed by the chemical industry (15%) and the metal working industry (7%).

The new legislation enacted in 2010 established the definition of contaminated sites together with reference values and provided a legal background for future prioritization studies and detailed investigations.

PROGRES IN MANAGEMENT IN CONTAMINATED SITES

From the analysis of contaminated sites management data, it can be concluded that preliminary studies on all identified potentially contaminated sites up to 2012 have been carried out, while main site investigations have been completed on a lesser number of sites (Tab. 1). Data sources on progress in the management of local soil pollution are represented by research and monitoring projects on soil and groundwater pollution from localized sources. These data are then used as input to the database managed by the Environmental Protection Agency. The results allow an assessment of which are the most dominant sources of local soil contamination.

The greatest number of registered sources of localized soil pollutions is related to municipal waste disposal sites (39.9%), oil extraction and production (28%) and industrial and commercial activities (10.8%) (Fig. 2 and 3). The database of potentially polluted and polluted sites does not include military sites. The number of sites in which manure are being stored is not reliable and for that reason it is not reported.

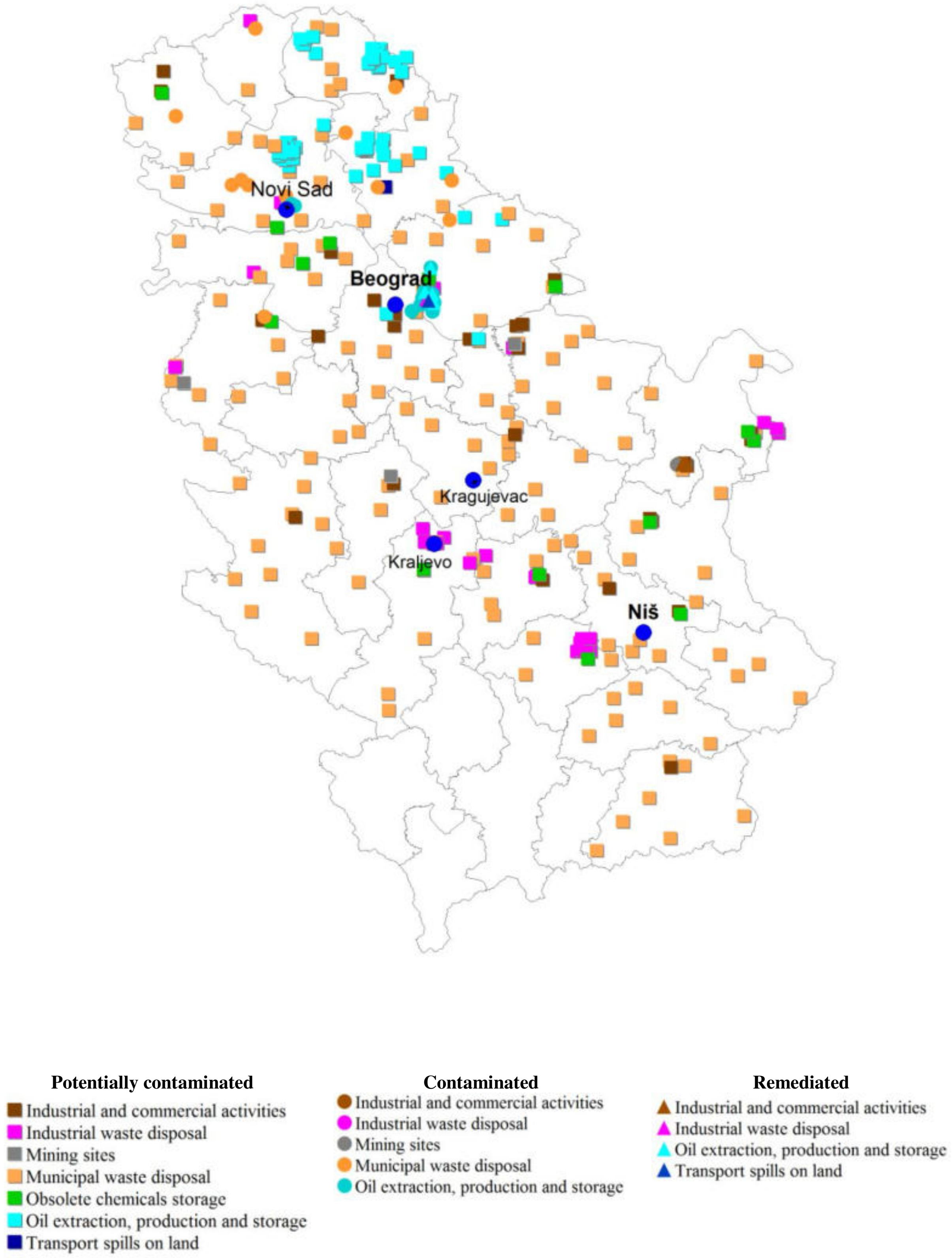

Fig. 1. Localized soil pollution sites

Tab. 1. Progress quantification in the management of local soil pollution

Number of sites	
Total number of sites	338
Potentially Contaminated	301
Preliminarily investigated	83
Contaminated	29
Main investigation	12
Remediated	8

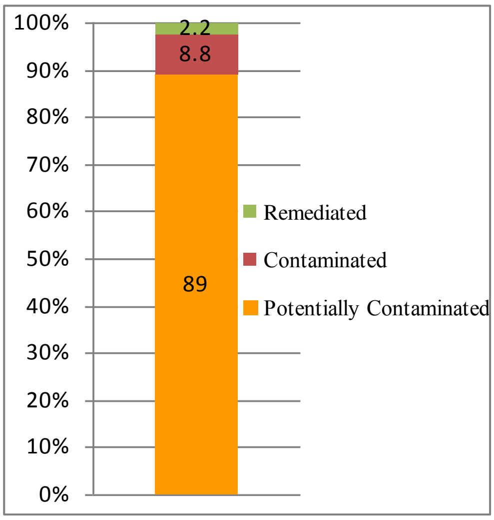

Fig. 2. Breakdown of quantification in management of local soil pollution

Open dumping and landfilling have represented the predominant method of waste management in the Republic of Serbia during the past decades. This practice resulted in over 3600 illegal waste disposal sites distributed all over the country. In most cases, illegal dumps are located in rural areas. They are primarily the consequence of the lack of resources to improve the quality of waste collection systems and of poor waste management organization at the local level. There are 147 landfills included in the Inventory that are being used by municipal public utility companies for waste disposal which represent a major potential soil and groundwater pollution source. The vast majority of disposal sites (up to 3300) are characterized by small deposition depth of waste and total waste volumes of less than 10,000 m^3. Only about 50 landfills in Serbia contain more than 100,000 m^3 of waste. These large landfills are responsible for more than 95% of the total CH_4 emissions from waste disposal, which was assessed as 60,000 tons of CH_4 in 2010 (Stanisavljevic et al., 2012).

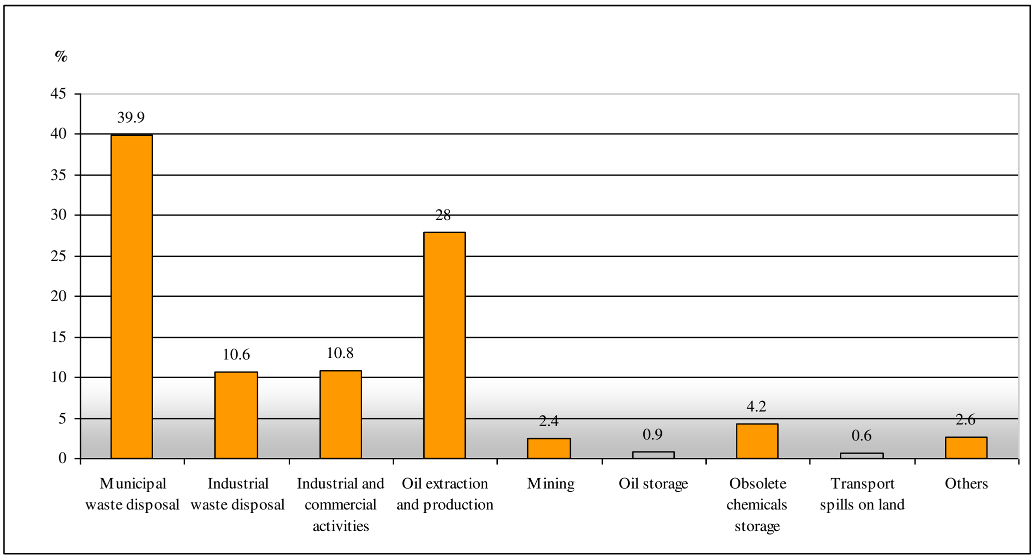

Fig. 3. Breakdown of activities causing local soil contamination [%]

The database of potential contaminated localities within the industry was updated in 2011. There were 189 potential contaminated industrial localities on the territory of the Republic of Serbia (Fig. 4). The greatest part of the identified polluted soil localities within the industry belongs to the oil industry (51%), followed by the chemical industry (15%) and the metal working industry (7%).

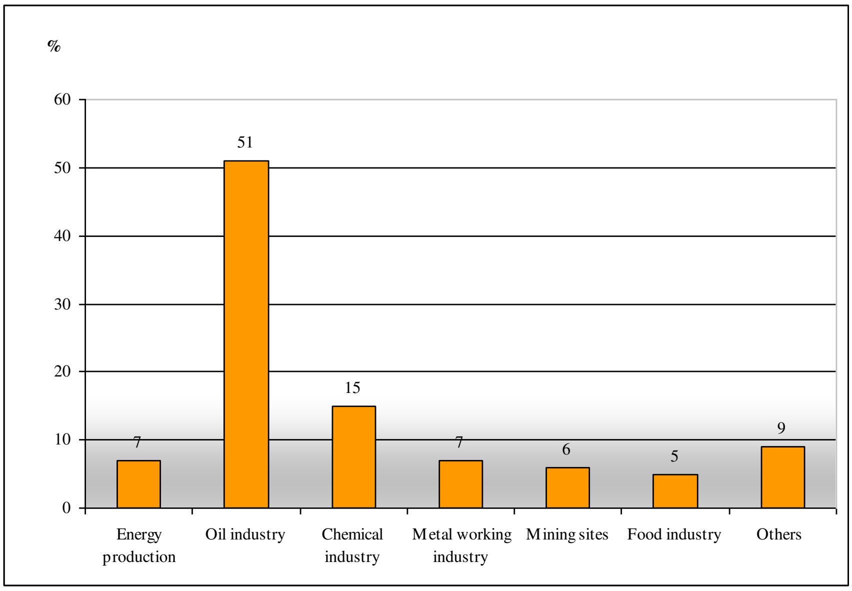

Fig. 4. Breakdown of industrial and commercial activities causing soil contamination (%)

There are different reasons for initiating risk reduction measures to manage local soil contamination in the Republic of Serbia. Considered 338 sites the prioritie for risk reduction measure is pressure to humans via drinking water (groundwater) (Fig. 5).

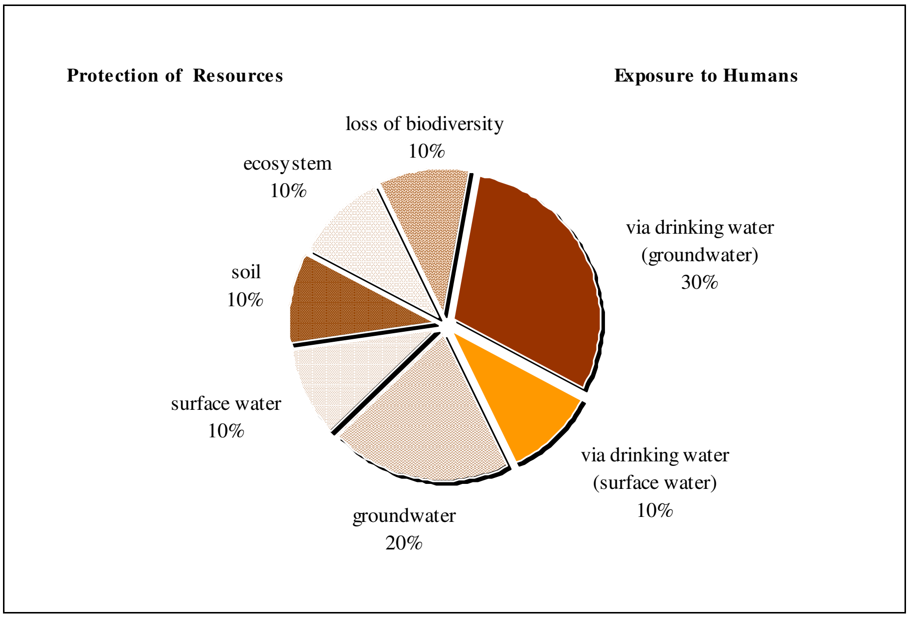

Fig. 5. Risk reduction priorities (%)

LEGAL FRAMEWORK FOR THE MANAGEMENT OF CONTAMINATED SITES

There is no special law on soil protection in the Republic of Serbia and the administrative capacities for the enforcement of existing laws and by-laws in this area are inadequate (Vidojevic, D., 2012). Soil management is accomplished by planning the sustainable use and conservation of soil quality and diversity, in accordance with environmental protection requirements and measures established by the Law on Environmental Protection, Law on Strategic Environmental Assessment, Law on Environmental Impact Assessment, Law on Integrated Pollution Prevention and Control (Official Gazette of RS, No. 135/04, 2004), and the Law on Amendments to the Law on Environmental Protection (Official Gazette of RS, No. 36/2009, Art. 22, No. 36/2009- other law 72/2009 - other law). The Law on Environmental Protection regulates soil protection and its sustainable use. Soil protection is accomplished by systematic monitoring of soil quality, monitoring of soil degradation risk assessment indicators and implementing programmes for the remediation of the consequences of soil contamination and degradation, whether natural or human-induced. Pursuant to the Law on Amendments to the Law on Environmental Protection (Article 16), legal and natural entities responsible for degrading the environment are obliged to remediate or otherwise restore the degraded environment, by means of restoration and remediation projects. Pursuant to the Law on Environmental Protection, in 2010 the Government of the Republic of Serbia adopted a Regulation on the programme for the systematic monitoring of soil quality, soil degradation risk assessment indicators and methodology for the development of remediation programmes. The Regulation is harmonized with the recommendations given in the Proposal for a European Soil Framework Directive – COM (2006) 232.

The adoption of this Regulation has provided the tools to ensure soil protection based on prevention of degradation - through identification of soil degradation risk areas, whether such degradation is natural or human-induced. The Regulation provides the basis for identification and management of contaminated sites in the territory of the Republic of Serbia. The level of chemical contamination of soil is assessed on the basis of limit values of contaminant concentration listed in the Regulation's Annex. In order to design contaminated soil remediation projects, additional studies to assess the level of soil contamination at the identified contaminated sites are carried out. According to the Regulation, the inventory of contaminated sites is an integral part of the environmental protection information system administered by the Environmental Protection Agency. Restoration and remediation priorities are identified on the basis of the Regulation which establishes criteria for the assessment of the status of highly threatened environment, the status of threatened environment and establishes criteria for the identification of restoration and remediation priorities (Official Gazette of RS, No.22/10, 2010).

The National Sustainable Development Strategy of the Republic of Serbia, the National Environmental Protection Program and the Spatial Development Strategy of the Republic of Serbia, represent the strategic background for soil protection in the Republic of Serbia. The strategic objectives of sustainable land use are given in the National Sustainable Development Strategy of the Republic of Serbia. The objectives include:

1. Harmonization of legislative acts related to land use and soil protection with EU legislation;
2. Prevention of further soil loss, especially due to industrial, mining, energy, communication and other activities, and conservation and enhancement of soil quality;
3. Prevention of soil degradation, changes of land use and development and management of agricultural soil.

In the framework of goals set up in the National Environmental Protection Program of the Republic of Serbia (2010), the goals related to the management of contaminated sites include rehabilitation of trash dumps - which are the greatest risk for environment - remediation of contaminated soils in industrial complexes and remediation and recultivation of areas degraded by mining activities. For the waste management planning, the Waste Management Strategy for the Period 2010–2019 was adopted in May 2010. This norm represents the basic document that provides conditions for rational and sustainable waste management in the Republic of Serbia, estimates the progress in waste management, lays down short-term and long-term objectives and provides conditions for rational and sustainable waste management.

CONCLUSION

According to the data on Inventory of contaminated sites collected by the Environmental Protection Agency, it can be concluded that:

1. Preliminary studies are conducted at most of the identified potentially contaminated sites in Serbia.
2. The greatest number of registered sources of localized soil pollution are related to municipal waste disposal sites, oil extraction and production sites and industrial and commercial activities.
3. However the data collected so far are not at the same level of quality at different locations, therefore it is not possible to estimate a comparable level of pollution at different potentially contaminated and contaminated sites.
4. The new legislation enacted in 2010 established the definition of contaminated sites together with reference values and provided a legal background for future prioritization studies and detailed investigations.
5. Additional and more detailed surveys are needed in order to update the inventory of all sites.
6. Resulting from these surveys, a National priority list for restoration and remediation of most polluted localities will be created.

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CONTAMINATED SITES IN THE CZECH REPUBLIC – GENERALISATION OF RESULTS FROM TRIAL INVENTORY OF PILOT AREAS

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KEYWORDS
Contaminated sites, inventory, classification, priority ranking, investigation, financing

ABSTRACT

Trial inventory of contaminated sites was carried out in three pilot areas of the Czech republic to test methodology and tools for intended national inventory of the whole country.

Inventory results from pilot areas enable some extrapolations concerning countrywide extent of this problem. Altogether, about 9 thousand of contaminated or potentially contaminated sites may be expected to issue as a result of the national inventory. Results of some sound pollution sampling will be available for not more than 20% of all sites.

For 80% of localities, there will be none or limited information on real character and extent of contamination. Their identification will be based primarily on site-use history information. Proposed and tested classification system will sort these sites with respect to their potential risk to public health and/or environmental protection interests. According to results from pilot areas, only about 12% of potentially contaminated (suspected) sites is supposed to be classified as representing eminent risk from this point of view. Thus, an effective allocation of effort and financial means for preferential investigation of these priority sites will be enabled.

The article deals also with question of securing finance for investigation of polluted sites in the present legislation and socio-economical situation of the country.

INTRODUCTION

A database of polluted sites is prerequisite for effective management of soil and groundwater pollution abatement, for protection of environmental and public health interests, for city planning. It is also important as an information source for public, for real estate transfers, etc.

To be reliable information source for all the purposes specified above, such a database must ideally originate from a countrywide and time-concentrated inventory campaign. Afterwards, the database must be continuously updated to keep its value.

PRESENT KNOWLEDGE ON POLLUTED SITES IN THE CZECH REPUBLIC

The SEKM database administrated by the Czech Ministry of Environment is presently the most extensive information source on polluted sites in the Czech Republic. It contains data on circa 7000 sites, but nevertheless, it is still far from giving a complete picture on the extent of the problem in the country.

New entries to the database come mainly from investigation and remediation companies that are obliged to submit data and results from their projects.

A systematic inventory of polluted sites covering the whole Czech Republic is still only in preparation (Suchanek, 2012).

PREPARATION OF THE NATIONAL INVENTORY OF POLLUTED SITES

So far, only development of methodology and tools for the national inventory campaign were completed as its introductory stage.

Developed methodology and tools underwent exhaustive testing. Trial inventory campaign was carried out in three pilot squares with the size 50 x 50 km each.

CLASSIFICATION OF POLLUTED SITES

Classification of all sites shall be an integral and important element (component) of the national inventory. The classification system officially issued by the Ministry of Environment was incorporated into inventory software tools (MoE, 2011).

The system sorts all sites into few basic categories according to the explicitly stipulated general type of further action that may be required or desirable with respect to character of the actual or potential pollution impact to public health, environment and/or to other interests (Tylcer et al., 2007).

For sufficiently investigated sites, a corresponding principle of necessary or desirable action for mitigation of site pollution impacts is derived from conclusions of investigation or risk analysis. An urgency of measure is also classified.

An investigation is the only logical further step for sites where existing information is not enough to make a final decision. For many sites, no information on contamination is available at all, but a suspicion issuing from a site use history must be taken into account. A simple and highly automatic scoring system classifies urgency for investigation of sites with lacking or insufficient information on pollution. The scoring is based on an assessment of: (1) character of presumed pollution, (2) site migration potential and (3) environmental sensitivity (vulnerability) of the site and its surroundings (Tylcer et al., 2007).

RESULTS FROM TRIAL INVENTORY AND THEIR GENERALIZATION

Total area of pilot squares for trial inventory represented one tenth of the whole Czech Republic expanse. The squares themselves were delineated by comparatively complex methodology to represent a certain "average" segment of the whole country with respect to natural conditions, population density and extent of industrial and agriculture activities.

Thus, it has been possible to exploit trial inventory results for deducting some extrapolation conclusions concerning the whole country (Marek and Szurmanova, 2011, Tylcer 2012).

There were altogether 897 sites identified in trial areas. Accordingly, circa 9 thousand of polluted or potentially polluted sites may be expected to exist in the Czech Republic.

Results of sufficient investigation enabling to evaluate pollution and its impacts were available for 18% of all sites only. On 79% of sites there was no sampling at all.

It means that at the end of the national inventory, about 80% of all sites will have still a status of a suspected locality only. Usage history will be the only reason to classify such sites as potentially polluted and put them into the database.

Without further investigation, we cannot know if there is really some pollution at all, what are its impacts and what mitigation measures would be adequate.

With respect to budget and other constrains, an investigation of all suspected sites within a short time is unrealistic. Costs for their appropriate investigation are estimated somewhere on the level of few billions Czech Crowns (more than 100 million Euros). Czech legislation does not enable to assign such investigation to an owner of suspected site in case he is not the polluter or his legal assessor that is a common case of sites with pollution from the past.

But as follows from trial inventory results, it may be expected that only about one tenth of all suspected sites will be classified as requiring investigation urgently (see fig.1).

This has an important practical impact. The countrywide inventory campaign with site classification will enable an effective identification of investigation priorities as a precondition for preferential allocation of effort and money for these sites.

About 6% of all sites are those for which a pollution mitigation measure is necessary or desirable. As could be expected, these sites single out themselves primarily from the group of sufficiently investigated sites (18% of all sites). One half of them have the highest classification as for the urgency of necessary mitigation measure. See fig. 1 for illustration.

Most of these sites are industrial plants or old landfills threatening groundwater public supply sources. Remediation is already under way on many of them.

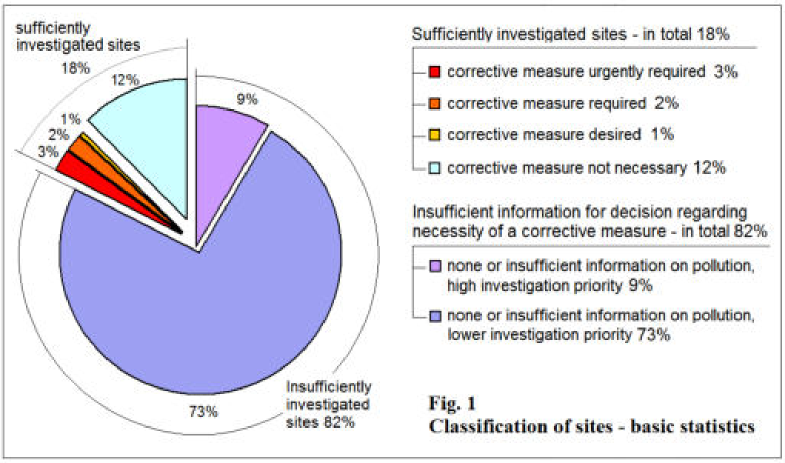

Fig. 1
Classification of sites - basic statistics

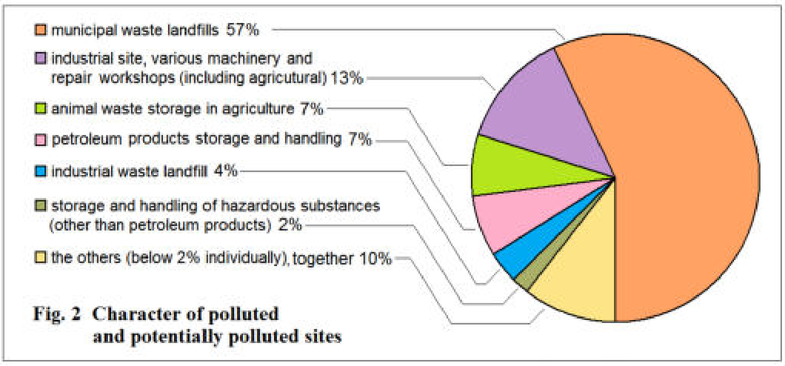

Fig. 2 Character of polluted and potentially polluted sites

Extrapolating results from testing areas to the whole country, we may expect there at least about 450 sites requiring some remedial action that will single out themselves from the minority group of sufficiently investigated sites. Another sites requiring some remediation will arise from the majority group of sites with lacking or insufficient data after their investigation is accomplished. It is difficult to estimate their number. It may be supposed that most of them will come from the group of sites with the highest classification as for the urgency of investigation.

As for the type of polluted sites, old municipal landfills highly prevail (57% of all sites). The second place belongs to industrial plants and various machinery or repair workshops including those in agricultural enterprises (13%). Significant portions hold sites with storage and handling of petroleum products (7%) and sites with storage of biological waste in agriculture (7%). See fig. 2 for illustration.

It looks that as for quantity of polluted or potentially polluted sites, the agriculture is comparable with industry. But presumably, majority of sites with the most severe pollution will belong to industry.

Results of trial inventory enabled also an assessment of importance of various information sources that could contribute to identification of polluted and potentially polluted sites.

OFFICIAL STATUS OF THE DATABASE OF POLLUTED SITES

As was told above, circa 80% of all sites are estimated to have a status of a suspected i.e. potentially polluted locality at the end of the national inventory campaign.
A "suspected site" might be perceived as a very sensitive term when private real estates are to be labelled in this sense in the public database.
To avoid any disputes, there must be very precise and juridically proof definition of the term "potentially polluted site" at the database home page. It must be explicitly specified that until a proper investigation is carried out to verify (for veryfying) real situation, the site history was the only reason to put the site into the database. On the other hand, without such an investigation, the site cannot be taken off it.
Then it would be on a site owner and in his own interest to commission the site investigation and to bear its costs to avoid problems in case he intends to go to a real estate market with his "suspected" site.

Thus, it is not necessary for the database to support its official status by some legal regulation. It could be enough the database is administrated by the Ministry of Environment and accessible through its official web page.

It could be a sufficient precondition for developing certain pressure on owners of suspected sites to investigate them without forcing them to do so by some new legislation. It is also a question if similar regulation forcing some private subjects to new duties and new expenditures would be passable for implementation in present Czech social atmosphere.

Present experience confirms it might work this way. From time to time, Czech Ministry of Environment faces to complaints and even legal action threats from owners of some sites that are in its present database of polluted sites. It confirms that a database is known to interested public and has its respect as a useful information source without having any official status.

Of course, the Ministry must not retreat to similar pressures from owners of suspected sites. In case it would do so, it could face to complaints from an opposite side - from subjects that would buy a property having been known to the Ministry as a suspected site but it had kept that information from public. Potential pollution might represent potential health risk for site users and the Ministry must not resign from its role of the guardian of public interests especially in case when human health could be in threatened.

CONCLUSIONS

So far, there has been not comprehensive information on polluted and potentially polluted sites in the Czech Republic.

According to results from trial testing of methodology and tools for a natinal invetory campaign, circa 9 thousand sites with pollution or potential pollution from the past may be expected in the whole country. For 80% of all sites, there will be none or unsufficent data on their real pollution. Their usage history will be the only reason to classify them as potentially polluted and put them into the database. Classification of these sites with respekt to their potential impact to surrounding environment will enable to identify priorities for prefferential investigation. Estimated costs for investigation of these high priority sites are about 15 million Euros while investigation of all sites with lacking data woud require much more than 100 million Euros.

Precise and juridically proof definition of the term "potentially polluted site" ought to prevent disputes from owners of these sites and to exert pressure on them to investigate their sites on their own costs in case they would intent to sell them.

Experience shows that there is a potential for the database to have a respect as a valuable information source for practice and for public without supporting its importance by some special legislation.

Of course, some official declaration of the database as the only and official information source on polluted sites could help (at least for several special purposes). But it would be risky to do so before the national inventory is carried out becasuse of possible disputes on responsibility of its (in)completeness.

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RISK PRIORITIZATION AND RISK ASSESSMENT AS A TOOL FOR MANAGING CONTAMINATED SITES

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KEYWORDS
simplified risk assessment, absolute risk assessment, management of large contaminated areas, megasites.

ABSTRACT

Risk assessment is considered a very useful tool in environmental policy because it promises a rational and objective basis for priority setting and decision making. A risk-based definition of “contaminated site” has been adopted in the proposal of the EU Soil Framework Directive, together with the provision of sites prioritization criteria in national remediation strategies based on risk evaluation. In the preparation of potentially contaminated sites and/or contaminated sites registers, risk assessment may help in setting priorities for environmental and human health protection in an objective and scientific way. Political and other management objectives may be considered separately. Absolute risk assessment, aimed at quantifying human health and or environmental risks associated to environmental contamination, is widely used as a supporting tool for contaminated land management, according to site-specific land uses. An increasing technical and research effort regards the application of “simplified” and “absolute” risk assessment procedures as support to the management of large contaminated areas and megasites. In this paper the results of two projects involving risk assessment application at large contaminated areas are briefly presented.

INTRODUCTION

The pollution of soil and groundwater caused by abandoned waste disposal sites and contaminated industrial areas is a complex environmental problem in all industrialized countries. Risk assessment is considered a very useful tool in environmental policy because it promises a rational and objective basis for priority setting and decision making. A risk-based definition of “contaminated site” has been adopted in the proposal of the EU Soil Framework Directive, together with risk based site prioritization criteria f within national remediation strategies. In an environmental context risk assessment is generally defined as the characterization of potential adverse effects of exposure of human and/or environmental receptors to hazards. It includes estimates of uncertainties in measurements, analytical techniques, and interpretative models (NRC, 1983). In contaminated land management, hazard is caused by the presence of contaminants in environmental media such as soil and/or groundwater. All risk assessment methodologies are based on the definition and parameterization of a Conceptual Site Model (CSM) on the basis of the source-pathways-receptor scheme. In the definition of potentially contaminated sites and/or contaminated sites registers risk assessment may help in setting priorities for environmental protection in an objective and scientific way. Political and other management objectives (e.g. economy) may be considered separately (Ferguson et al, 2001). To this purpose, a “simplified” or “relative” risk assessment procedure is generally adopted not aimed at quantifying risks associated to site contamination, but rather at comparing sites on the basis of a risk scoring system. Risk scores assigned to sites allow for site ranking, in order to decide about resources allocation and priorities of action in terms of detailed site investigation at potentially contaminated sites or remedial/safety measures at already identified contaminated sites. Absolute risk assessment, aimed at quantifying human health and/or environmental risks associated to environmental contamination, is widely used as a supporting tool to contaminated land management, according to site-specific land uses. Risk assessment procedures usually start when, after a preliminary study, a confirmed presence of pollutants has been identified in soil or groundwater. A further investigation may be carried out, and contamination levels are compared with soil and groundwater risk-based criteria (e.g. screening levels). These criteria may be generic, based on general and conservative assumption in CSM parameterization , or may be derived from site-specific data and models used to predict adverse effects of pollution and the need for remediation.

An increasing technical and research effort regards the application of “simplified” and “absolute” risk assessment procedures within the management of large contaminated areas and megasites. These areas are generally characterized by a wide extension, multiple and differentiated sources, different land uses and may need a large amount of information to identify real pollution problems and remediation needs. Both “simplified” and “absolute” risk assessment procedures , may ,at different levels, support the focusing of actions (further investigation and/or remedial actions) on “critical areas”. In this paper the results of two projects involving risk assessment application at large contaminated areas are briefly presented: 1) the project “Towards an EEA Europe-wide assessment of areas under risk for soil contamination”, aimed at the identification of problem areas for soil contamination in Europe and including the PRA.MS “simplified” risk assessment model, 2) the preliminary application of “absolute” risk assessment to the wide potentially contaminated area of Portoscuso municipality in south-west Sardinia.

THE EEA PROJECT FOR THE IDENTIFICATION OF PROBLEM AREAS

From 2004 to 2006 the EEA (European Environment Agency) has developed the project “Towards an EEA Europe-wide assessment of areas under risk for soil contamination”. The main objectives of the activity were to assess location and extent of potential problem areas of suspected/contaminated sites in Europe and to characterize/classify these areas according to their complexity, sources, receptors and contaminants. The results supported a broad assessment of the state of soils in Europe. In fact problem areas may be candidates for detailed monitoring at the European level (EC, 2004). For the scope of the project, a working definition of problem areas was adopted, based on preliminary risk assessment criteria. More specifically, problem areas for soil contamination are defined as:

“*Areas where soil contamination is considered to pose significant risks to human health and/or ecosystems with impacts beyond the local environment and where the assessment and reporting of pressures, state, impacts and remediation activities is of relevance at the European level. In particular, these are areas where:*

- *potential soil polluting activities are currently located or have been located in the past. This activities are included in a pre-defined list;*
- *the size of the site is above certain thresholds in terms of emission and waste volumes, site area, volume of operations and so on;*
- *the estimated risks to human health and/or ecosystems, resulting from the application of a preliminary risk assessment model, are above certain thresholds.*”

The project included the following activities:

a) Review and analysis of available methodologies for the prioritisation and identification of contaminated sites, which use a preliminary risk assessment approach. The results of the review are included in the technical report ‘Review and analysis of existing methodologies for preliminary risk assessment’ (EEA, 2005a).
b) Analysis and selection of available data on potential problem areas at the EU level.
c) Analysis and selection of geo-referenced environmental data available at the EU level relevant to the risk-based identification of problem areas.
d) Development of a tiered preliminary risk assessment model (PRA.MS) (EEA, 2005b).
e) Application of the tiered model to selected sites, using available data (EEA, 2005c).
f) Proposal of a methodology for the identification of potential problem areas and for the presentation of the results of the assessment.
g) Development of the assessment and graphic presentation of the results, including uncertainties.

The PRA.MS (Preliminary Risk Assessment Model for the identification and assessment of problem areas for Soil contamination in Europe) model consists of two tiers, Tier 1 and Tier 2, that can be applied in sequence or alternatively. Both tiers lead to an assessment and classification of sites using risk scores (Figure 1).

The application of Tier 1 leads to a ‘suggestion’ of potential problem areas, to be confirmed by further data collection and Tier 2 assessment. Tier 1 is less accurate than Tier 2, since it can be run with low resolution and very generic data when detailed data are unavailable. In addition, a Tier 0 has been included for pre-selecting sites from available and relevant European databases, in order to reduce the number of sites to be processed and to screen out those sites that, according to specific criteria, are not of EU concern and not relevant to the project. Tier 0 is based exclusively on ‘site-specific’ criteria.

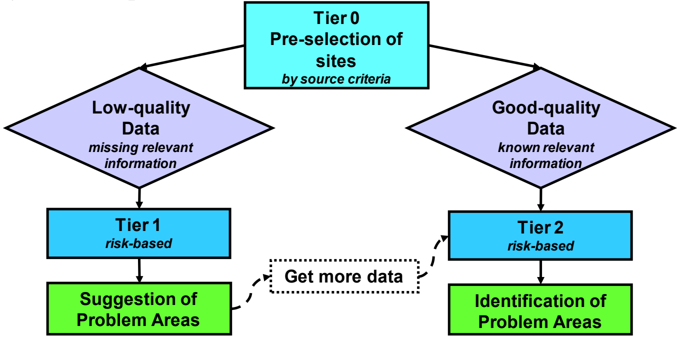

Fig. 1. PRA.MS tiered approach for the identification of Problem Areas

For the development of the PRA.MS model a review and analysis of 27 existing and documented international methodologies used in member countries and overseas (at national, state or regional level) for the prioritization and planning of soil remediation and protection programs. The scheme adopted in the analysis follows the conceptual approach "Source-Pathway-Receptor" that generally characterizes any contaminated sites risk assessment procedure . In this context, parameters used by each methodology have been listed under the S-P-R main risk assessment elements. The human health risk scenario and generic conceptual model include four exposure routes to potential human receptors to soil contaminants: Groundwater (GW), Surface water (SW), Air (AIR), Direct contact (DC). Groundwater and surface water are considered here as pathways and exposure routes of soil contaminants to human receptors. The ecological risk scenario includes two potential receptors of soil contamination: Surface water (SW) and Protected Areas (PA). Surface water is considered here as an ecological receptor. PRA.MS then adopts a mixed additive and multiplicative algorithm for the calculation of the overall site risk score:

- parameters are aggregated or represented by factors and the factors are scored on the basis of parameter quantitative or qualitative values;
- factors, in turn, are grouped by Source-Pathway-Receptor indicators and weighted depending on the relative importance in describing the indicator; factor scores are added up in order to score each Source-Pathway-Receptor indicator;
- S-P-R indicator scores are then multiplied for each of the four exposure routes (GW, SW, AIR, DC) in human health risk assessment and for each ecological receptor (SW, PA) for ecological risk assessment;
- exposure route/ecological receptor scores are calculated;
- overall risk score is given by the root mean square of all exposure routes/ecological receptors scores.

Parameters have been chosen through the analysis, comparison and harmonisation of the most common parameters used in the examined methodologies and existing databases at EU level. The parameters considered in the Tier 1 model are a subset of parameters taken into account in the Tier 2 model. Both assessment levels envisage the use of site-specific data or, when these are not available, aggregated GIS data or 'proxy' data. When input data are not available, a reasonably conservative estimate of the factor score is envisaged. This feature, as well as well as the use of proxy and low-resolution GIS data, is taken into account in the uncertainty assessment. The approach adopted for dealing with uncertainties leads to conservative assumptions - large site scores - in case of low quality information. This condition is identified by high uncertainty score values that are calculated separately from risk scores. The system design is such that sites analyzed under Tier 1 assessment should result in higher uncertainties than sites analyzed in Tier 2.

The PRA.MS approach has been tested by application to a selection of mining and industrial sites for which data were available at EU level. The part of the model dealing with ecological risks was not considered due to lack of data and time resources. Site-specific data available on mining sites included in the DECHMINUE database (BRGM, 2001) were processed according to Tier 2 of procedure, while site data from the European Pollutant Emission Register of emissions from industrial facilities (EPER; European Commission, 2000) database were processed according to Tier 1 model procedure. Information on climate, soil, slope, rivers and lakes, land use and natural/protected areas from which proxy data were derived was extracted from other European databases, such as CORINE Land Cover 2000 and the Soil map of Europe 1:1000000. The results of the assessment on a selection of mining sites showed that no regional trends on health risks were observed. In fact the majority of high-risk scores sites were closed or abandoned mines where rehabilitation had not yet taken place. In these sites, release of contaminants to surface water and air had often been observed and documented (Figure 2). The nature of most hazardous (or most toxic) chemicals present at mining sites has a strong influence on overall risk score. Leaching of contaminants through the soil to groundwater bodies and drinking of contaminated groundwater represent the most relevant exposure route, because it contributes more than others to the overall risk associated to each site. Secondary routes include surface water, direct contact and air. Uncertainty is high in assessing the contribution of groundwater and surface water exposures routes to the overall site risks, mainly due to data gaps. This implies that good basic information on these routes is required at the European scale.

Tier 1 assessment on EPER industrial facilities showed that the greater risk to human health seems to be related to contamination through surface water, although it only represented a limited number of sites (1%). Installations for the production of biocides and explosives presented the highest risk. On the other hand, waste disposal sites had the lowest risks, which can be related to the more stringent National and European legislation regulating this specific activity (Figure 3). A peer review process suggested to improve the methodology by including: a pre-screening level in order to better focus the assessment and limit data collection requirements; an assessment of multiple risks and multiple sources; a sensitivity analysis of the required parameters; availability of data sources of better quality and resolution, finalization of ecological risks assessment, application of the methodology to a selection of sites using data provided by national experts and covering a wider range of sites of EU relevance. In particular the need of a pre-screening step for the identification by each MS of candidate areas for PRA.MS application, derived from the difficulty of setting a “common” and “generalised” criteria and procedure to be applied in the context of different national contaminated land management procedures.

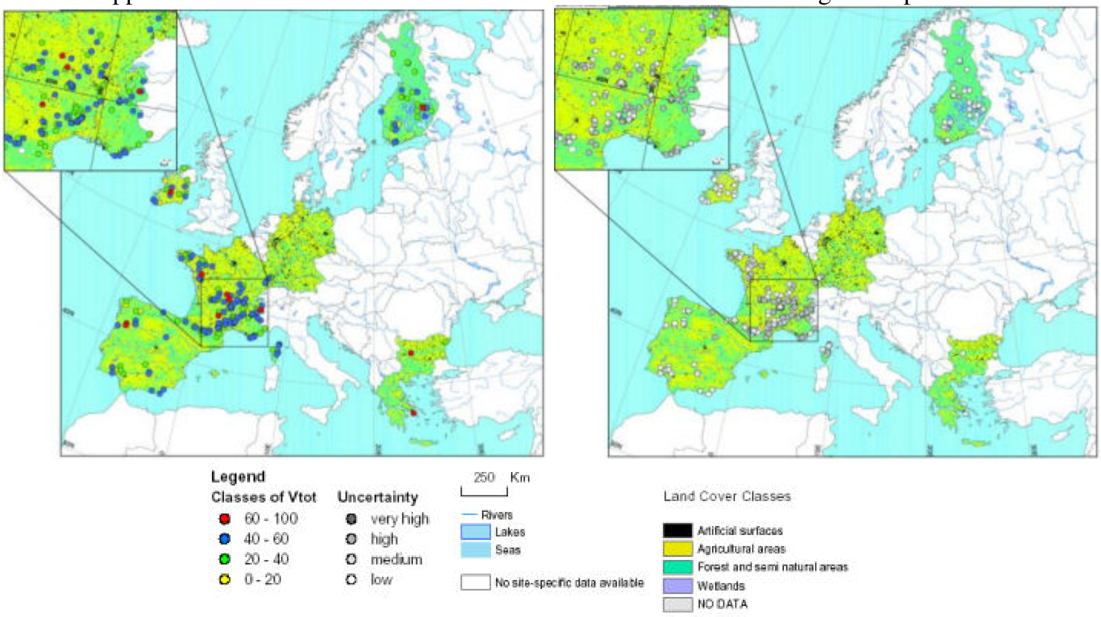

Fig. 2. Results of PRA.MS application to a selection of mining sites (Note: The assessment shown in this map refers to a selection of sites, chosen on the basis of data availability. Therefore, it should be considered as preliminary) processed by APAT/ETCTE - © EEA 2004

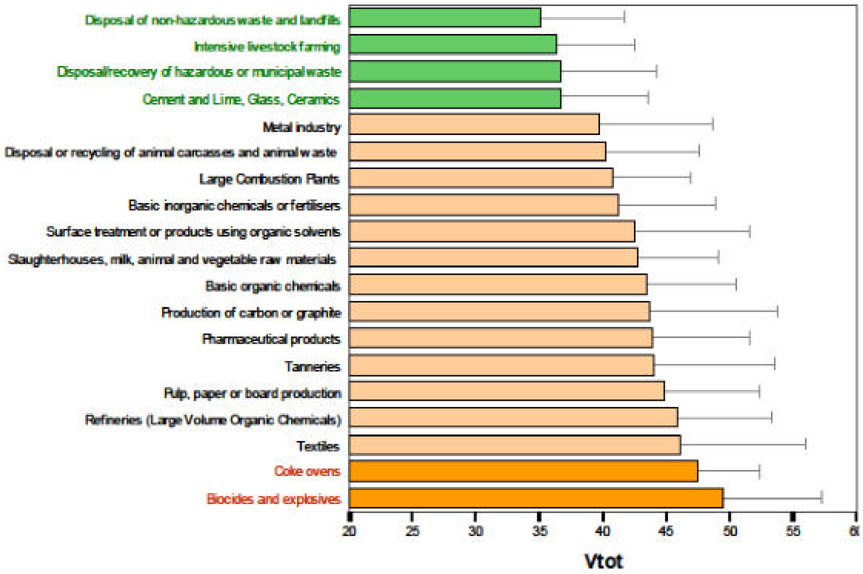

Fig. 3. PRA.MS overall Tier 1 risk scores (Vtot) by facility according to IPPC classification. Bar shows mean + SD. Homogenous groups are represented in different colours (p = 0.01, n = 7803) processed by APAT/ETCTE - © EEA 2004.

APPLICATION OF SITE SPECIFIC RISK ASSESSMENT TO PORTOSCUSO MUNICIPALITY

The potentially contaminated area of Portoscuso Municipality (South-West Sardinia, Italy) has been included in the National Priority List Site “Sulcis Iglesiente Guspinese” for the presence of a large metallurgic industry district, the Portovesme industrial area, including also a coal and fuel oil combustion power plant and some waste disposal sites (big disposal area of red muds resulting from bauxite refining process; metallurgic waste disposals; disposal of ashes from the combustion plant). The surrounding areas are mainly used for agricultural purposes (production of vegetables and vineyards)and two residential agglomerates (Portoscuso and Paringianu) and a nature valuable area (Boi-Cerbus Lagoon) are also present. The conceptual model of soil contamination indicates a diffuse passive contamination mainly caused by emissions from the industrial district and contaminated soil may be the primary source of groundwater pollution up gradient the Portovesme area (APAT, 2008). However, the geological and hydrogeological context indicates also a natural geochemical contribution to the diffuse presence of inorganic substances (metals, metalloids and other inorganics) in soil and, to a minor extent, in groundwater. The whole municipal territory outside the industrial area (30 km^2) has been investigated from July 2009 to March 2010 with the collection of 308 top soil (0-0,1 m) samples (TS), 371 surface (0-1 m) and deep soil samples (>1m) (SS and DS) and 78 groundwater samples from monitoring points. Results of the investigation in the areas surrounding the industrial district confirmed a diffuse presence in soil of heavy metals (As, Cd, Hg, Pb, Sn, Zn) above the screening values all over the investigated area. Limited presence in few samples for Cu and V has been recorded. For some of the diffuse elements (Zn, Pb and Cd), the contamination pattern is characterized by an impressive trend decreasing with sampling depth. This is indicative of a surface soil contamination mainly due to fallout from the industrial district, while in deep soil the presence of contaminants may be correlated to natural background. For As the diffuse presence in soil seems to be originated from background (Figure 4). For Hg, Cu and V it is not possible to define a clear origin.

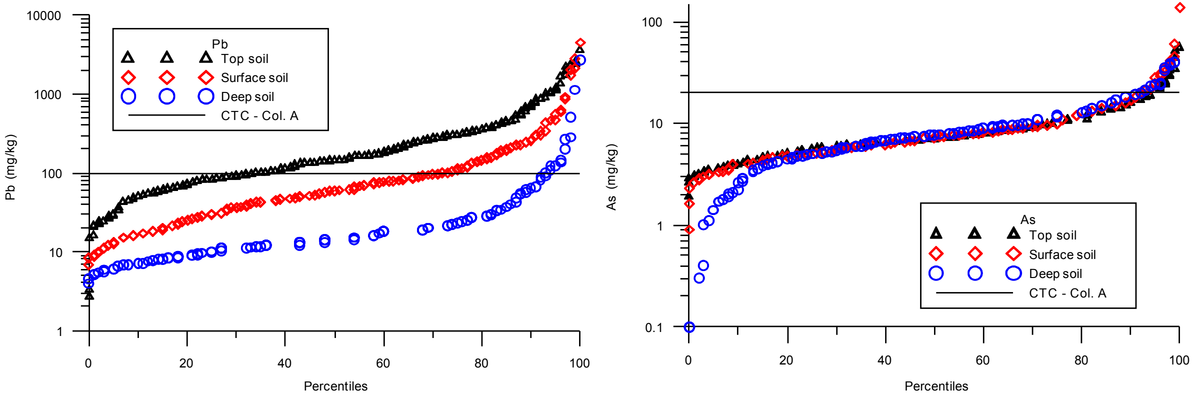

Fig. 4. Portoscuso vertical contamination pattern of Pb and As. The significant decreasing of Pb concentration with depth is emphasized. The depth-non sensitive pattern is reported for As whose origin is not related to fall out from industrial district.

According to the Italian legislation on contaminated sites management (Legislative Decree 152/06), a site-specific human health risk assessment has to be carried out in order to assess the need for remediation also outside the industrial district. The major problem in the application of risk assessment to a diffusely polluted large area, is to account simultaneously for the spatial distribution of soil contamination and for the land use. In case of a diffuse presence of contaminants in soil, point data may be associated to a wider area identified with Thiessen polygons on the basis of the sampling strategy. Within each Thiessen polygon it is reasonable to consider a uniform chemical concentration in each homogeneous soil layer (top soil, surface soil, deep soil). Given this conservative assumption on contamination spatial distribution, the differences in human exposure depend only on land use. For the assessment of risks to groundwater resources associated to soil contamination, the geological variability within each Thiessen polygon should be accounted for (Figure 5). These assumptions are generally the basis for the application of "preliminary" risk assessment methodologies. On the basis of land use within the Thiessen polygon, different sub-areas for human exposure evaluation are defined, while for the evaluation of soil-to-groundwater leaching pathway an "average" geological setting is defined taking into account the properties of the different lithologies weighted on the surface of the emerging layers. The conceptual model adopted on the basis of land use is indicated in Table 1.

Tab. 1. Conceptual model for human health risk assessment and for groundwater protection

Scenario according to land use	Pathways	Receptors
Residential Residential + Agricultural activities	Direct contact (for TS only) Outdoor vapor and powders inhalation (for SS and DS) Indoor vapor inhalation (for Hg in SS and DS only)	Adults and Children
Industrial Commercial Agricultural activities	Direct contact (for TS only) Outdoor vapor and powders inhalation (for SS and DS) Indoor vapor inhalation (for Hg in SS and DS only)	Workers
Naturalistic (recreational)	Direct contact (for TS only) Outdoor vapor and powders inhalation (for SS and DS)	Adults and Children (exposure frequency reduced to 1,5 hr/day)
Pasture activities	Direct contact (for TS only) Outdoor vapor and powders inhalation (for SS and DS)	Adults and Children (exposure frequency reduced to 1,5 hr/day)
Groundwater protection	Soil to groundwater leaching form surface	Compliance with GW target values

Therefore the proposed approach adopted a parameterization of source geometry and exposure scenarios more conservative than the traditional risk assessment, that is generally limited to the scale of a single area defined by property boundaries. This methodology is more similar to a "generic" and "simplified" risk assessment, even if many parameters (organic carbon content, soil/water partition coefficient, hydraulic conductivity, soil texture) have been derived from site specific measurements (ISPRA, 2010). The results of risk assessment identified large portion of the studied area as not contaminated (i.e. no longer posing significant risks to human health and/or the environment). However in some residential areas, or areas where the agricultural scenario has been integrated with the residential one, the Risk Threshold Concentrations (RTCs, derived from the site-specific risk assessment, indicating non acceptable risks) of Pb, Cd, and As were exceeded. For Pb, Cd, and As critical pathways are direct contact with TS and soil to groundwater leaching for SS and DS. For Hg critical pathways are indoor and outdoor air inhalation.

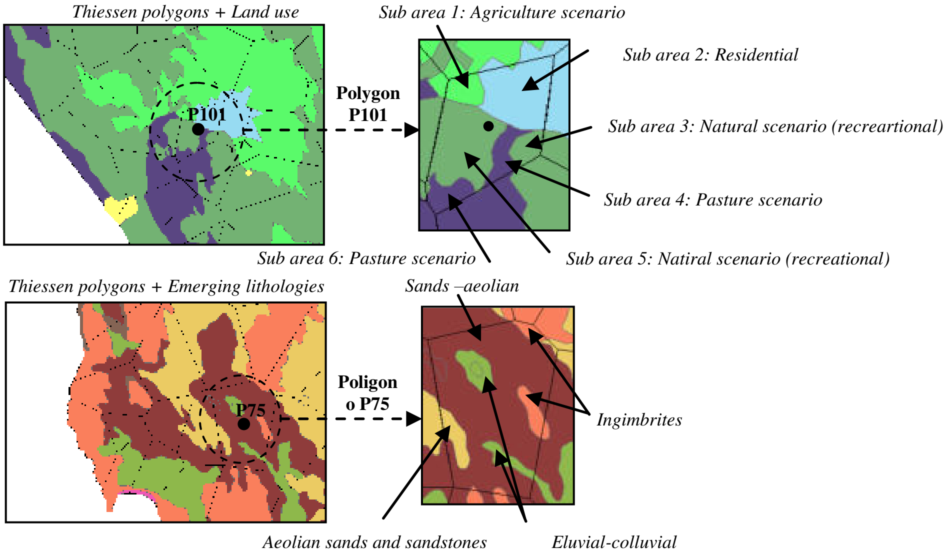

Fig. 5. Methodology for the evaluation of spatial soil contamination together with land use (human exposure) and geological setting (groundwater protection) at Portoscuso site.

A detailed investigation in critical sub-areas (sub-areas where RTCs are exceeded) identified in the first stage of risk assessment is planned in order to better investigate within each critical sub-areas on: distribution of contamination especially for areas where no soil sample is available, exposure conditions (e.g. real residential use also in agricultural areas, presence or planning of buildings), presence of volatilization and leaching transport pathways with leaching tests, soil gas and flux chambers sampling. A second stage of risk assessment will be applied on the basis of the detailed investigations.

CONCLUSIONS

In the management of contaminated sites risk assessment has proven to be a very useful tool for identification of contamination and planning soil remediation. The results of application of “simplified” and “detailed” risk assessment to large contaminated areas may help in orienting actions to “critical” or “problem” areas. The “harmonization” of risk assessment methodologies envisaged by the Soil Thematic Strategy and the proposed Soil Framework directive is still a critical issue due to the difficulty to set a “common” procedure especially for large areas/megasites management. A flexible proposal of a “toolbox” of different risk assessment methodologies clearly describing the applicability, the advantages and the limitation of each tool, may be a good compromise.

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MANAGEMENT OF CRUDE OIL CONTAMINATED LAND IN RUSSIA USING A RISK ASSESSMENT APPROACH

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KEYWORDS
Crude oil, contaminated sites, land management, risk assessment, bioremediation

ABSTRACT

Land contamination with crude oil presents a serious environmental problem for oil-producing regions in Russia. Crude oil and petroleum products are ubiquitous soil and groundwater pollutants resulting from spillage from producing wells, storage tanks and damaged pipelines. Our research is directed to provide the site-specific risk assessment and to improve response actions to terrestrial oil spills, including biological clean-up technologies. A conceptual model for the land oil-spillage from a disrupted pipeline was applied in the source-pathway-receptor risk assessment to characterize the fate and transport of petroleum hydrocarbons under various climatic, soil, and hydrological scenarios. Based on risk assessment results, target crude constituent concentrations in soil were determined to be achieved during remediation actions. Selected bioremediation strategies were tested at pilot scale, including bioaugmentation with hydrocarbon-oxidizing bacterial cultures immobilized onto hydrophobized sawdust and amendment with a biosurfactant for the *ex-situ* site treatment, which resulted in efficient oil degradation and reduction of soil ecotoxicity.

1. INTRODUCTION

Crude oil and petroleum products are widespread soil and groundwater pollutants resulting from spillage from the storage tanks and damaged pipelines. There are thousands of sites that have been seriously contaminated by petroleum products in oil-producing regions around the world [1]. For Russia and the former Soviet Union, reliable data are difficult to find. In 2003, the World Bank published a report on pipeline failures in the countries of the former Soviet Union. The data search identified 113 major crude oil spill accidents during the period 1986–96 (inclusive). Just under 90% of these occurred in Russia. Whilst corrosion was still a major cause, there were double the number of spills caused by mechanical failure and illegal pipe distruction. According to the Russian Federation State Environment Report, in 2003 losses of Russian oil and gas companies were approximately 3% from the product transported [2]. Oil spillage from disrupted pipelines is a major threat in large oil producing regions, e.g. Urals and Siberia, which are characterized by seasonal weather extremes and especially cold winters. Crude oil is a complex mixture that contains many toxic and carcinogenic compounds such as benzene and polycyclic aromatic hydrocarbons. They are toxic to most forms of life and can also have serious consequences for human health. Many existing remedial technologies are inappropriate to Russia's size and cold climate and energy-intensive technologies like incineration are not feasible for such large territories. Alternatively, biological remediation methods for oil-contaminated soils have gained increasing popularity due to their sustainability, relative cost-efficiency and environmental safety. The present paper describes a risk based approach to the management and bioremediation of crude oil contaminated site under cold climate conditions in the Ural region of Russia.

Harmful effects of oil spills on natural environments have been extensively studied. However, only few studies so far have focused on the effect of oil exposure on human health [3]. This supports the need for appropriate risk assessment methodology for human populations exposed to spilled oils, including the workers involved in the cleanup, in order to evaluate not only possible immediate consequences for their health but also the medium- and long-term effects, and the effectiveness of the protective devices used. Risk assessment is a widely accepted strategy for contaminated land management. The rising contamination problem, cost of remediation, and scientific questions about the real threat posed by crude oil contaminated land to human health have driven the development of risk-based environmental assessment criteria for soils and groundwater. The shift to risk assessment approach and suitability for use criteria decreases the cost burdens, and has also been a factor in the development of new remedial technologies, including bioremediation. Many countries have developed or are currently developing procedures and guidelines for assessing the risks posed by contaminated sites. It should also be noted that for petrochemical- and crude oil-contaminated sites, quantitative risk assessment is made more challenging by the complexity of the contaminant mixture [4] and the effects of weathering on the bioavailability of risk-critical compounds. It is common for high heterogeneity to exist in the distribution of hydrocarbon contaminants, which impacts risk assessment results and the success of further remediation actions. For heavier fraction hydrocarbons such as paraffines and polycyclic aromatic compounds, losses due to biotic and abiotic weathering processes may result in compounds with increased hydrophobicity and recalcitrance [5]. These compositional changes dramatically affect the bioavailability and bioaccessibility of risk-critical compounds.

In this paper, a conceptual model (Fig. 1) for the terrestrial oil-spillage from a disrupted pipeline occurring near a river was used in the source-pathway-receptor risk assessments. It is widely accepted that modelling is a powerful tool for integrating various elements in risk assessment such as site characterization, contaminant fate and transport, exposure assessment and risk calculation. However, such models are abstract and simplified representations of complex systems and are based on numerous assumptions and approximations. It is therefore important that models are validated and tested in real-life situations, either as part of oil-contaminated land risk assessments or in remediation projects. At present, about 20 human health risk assessment models are developed worldwide [6]. Many of the models have comparable approaches to assess health hazards arising from polluted soils, and most programs apply similar EPA algorithms to calculate carcinogenic and non-carcinogenic risks [7]. However, the input parameters and scenarios considered in various models are different [8]. Moreover, national risk and remedial standards vary significantly through the world. Results obtained with different risk assessment methods are therefore often not comparable [9]. Actually, land management and remediation organizations in different countries usually utilize the models developed in particular country using national language and national environmental standards. This is particularly true for Russia, where two program systems, EHIPS (Environmental Health Information Processing System) developed in the Space Research Institute, Moscow and "Ecolog" (Unified Program for Air Contamination Calculation) developed by Integral, St.-Petersburg were designed for the assessment of human health risks from air contaminations. Both risk assessment systems function in Russian, so they are available to a wide range of national environmental managers. We have developed a risk assessment system "Eco-Risk" for crude oil and other hydrocarbon contamination (RF State Registration No. 2011611923), which realizes multimedia, multipathway and multireceptor approach and can be used for the land management and remediation purposes.

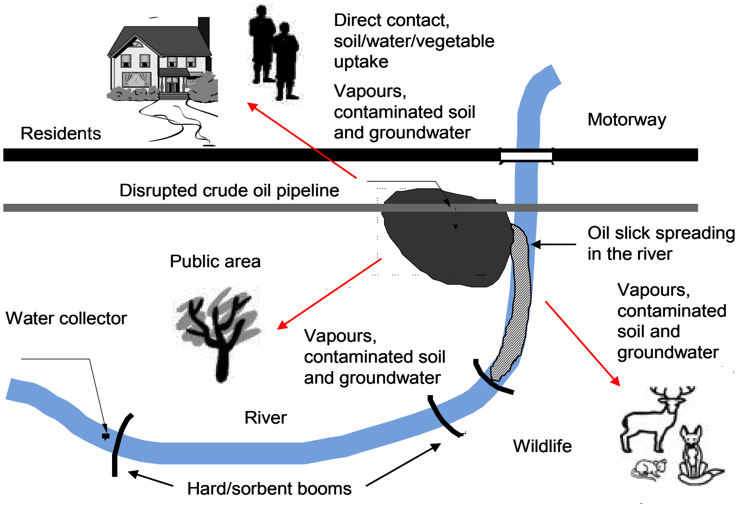


Fig. 1. Risk assessment model for crude oil spillage from a disrupted pipeline.

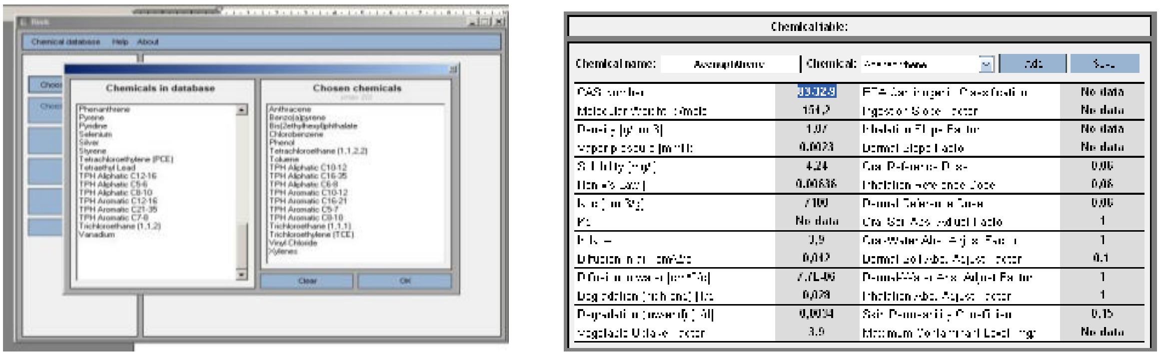
2. RESULTS

The "Eco-Risk" program has been developed for estimating human health risks from petroleum hydrocarbon (PH) contamination, which has following steps (Fig. 2) and functions (Fig. 3):

- database maintenance for PHs;
- calculation physical quantities related to the spread of PHs on the ground;
- convenient presentation of results;
- calculation of human health risk;
- calculation of probable PH concentrations based on hazard index and carcinogenic index.

Step. 1. **Choose chemicals**

PHs of concern can be selected from the database, which by default contains 79 chemicals and can be expanded. New chemicals can be added to the database as well as some chemicals can be deleted from it. For each chemical stored, 28 parameters used to calculate the fate and transport models and health risk.



Chemicals in database

Phenanthrene
Pyrene
Pyridine
Selenium
Silver
Styrene
Tetrachloroethylene (PCE)
Tetraethyl Lead
TPH Aliphatic C12-16
TPH Aliphatic C5-6
TPH Aliphatic C8-10
TPH Aromatic C12-16
TPH Aromatic C21-35
TPH Aromatic C7-8
Trichloroethane (1,1,2)
Vanadium

Chosen chemicals

Anthracene
Benzo(a)pyrene
Bis(2ethylhexyl)phthalate
Chlorobenzene
Phenol
Tetrachloroethane (1,1,2,2)
Toluene
TPH Aliphatic C10-12
TPH Aliphatic C16-35
TPH Aliphatic C6-8
TPH Aromatic C10-12
TPH Aromatic C16-21
TPH Aromatic C5-7
TPH Aromatic C8-10
Trichloroethane (1,1,1)
Trichloroethylene (TCE)
Vinyl Chloride
Xylenes

Fig. 2. Flow diagram of health risk assessment

Step 2. **Select contaminated media, F&T model and pathways**

The model developed involves 5 media:

1. Soil
2. Indoor air
3. Outdoor air
4. Groundwater
5. Surface water

There are 9 fate and transport models used:

1. Vapor model from groundwater
2. Johnson & Ettinger model
3. Dominant Layer model
4. Vadose zone soil to groundwater
5. Saturated zone soil to groundwater
6. River mixed with groundwater vadose zone model
7. River mixed with groundwater saturated zone model
8. Lake mixed with groundwater vadose zone model
9. Lake mixed with groundwater saturated zone model

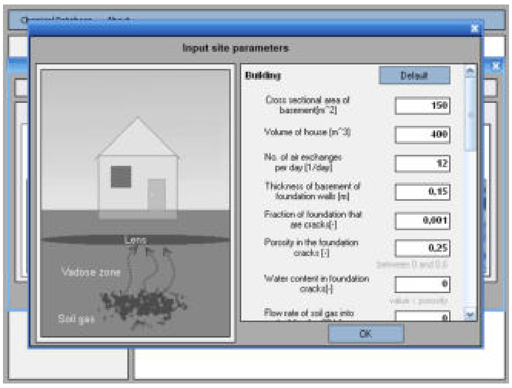
There are 14 pathways:

1. Ingestion of contaminated soil
2. Dermal contact with soil
3. Ingestion of vegetables grown in contaminated soil
4. Ingestion of groundwater used for indoor
5. Dermal contact with groundwater used indoor
6. Inhalation in the shower
7. Ingestion of groundwater used for irrigation
8. Inhalation of volatiles from irrigation groundwater
9. Dermal contact with water spray
10. Ingestion of vegetables irrigated with groundwater
11. Ingestion of surface water
12. Dermal contact with surface water
13. Inhalation of indoor air
14. Inhalation of outdoor air

Chosen chemicals:
- Anthracene
- Benzo(a)pyrene
- Bis(2ethylhexyl)phthalate
- Chlorobenzene
- Phenol
- Tetrachloroethane (1,1,2,2)
- Toluene
- TPH Aliphatic C10-12
- TPH Aliphatic C16-35
- TPH Aliphatic C6-8
- TPH Aromatic C10-12
- TPH Aromatic C16-21
- TPH Aromatic C5-7
- TPH Aromatic C8-10
- Trichloroethane (1,1,1)
- Trichloroethylene (TCE)
- Vinyl Chloride
- Xylenes

Human Health

Soil:
-Fixed Concentration



Cross sectional area of basement[m^2] 150
Volume of house [m^3] 400
No. of air exchanges per day [1/day] 12
Thickness of basement of foundation walls [m] 0,15
Fraction of foundation that are cracks[-] 0,001
Porosity in the foundation cracks [-] 0,25
between 0 and 0.6
Water content in foundation cracks[-] 0
value < porosity
Flow rate of soil gas into 0

Step 3. **Determine receptor point concentration**

There are two methods for determining receptor point concentration: (i) enter receptor point concentration or (ii) enter concentration in the source and use F&T model to calculate receptor point concentration.

There are two ways to enter the concentration: (1) single value or (2) sample database.

1. Single value is used when a point value is known. In this case you need to enter one value for each selected chemical.

2. Sample database is used to summarize site data and calculate means as input for model. The program supports four methods for averaging: arithmetic, geometric, 95th Upper Confidence Level Normal, weight factors. When F&T model is used, it requires entering site-specific parameters, a set which depends on the model. In several cases it is also required to enter specific values of chemical parameters, such as degradability or degradation rate

Step 4. **Describe the receptors**

Four types of receptors are incorporated in the model: Adult, Child, Worker and Trespasser. Default set of parameters developed for Reasonable Maximum Exposure (RME) and typical exposure, which can be changed for every case.

Step 5. **Risk calculation**

The program calculates carcinogenic risk and non- carcinogenic hazard index using the equations proposed by US EPA. First step of risk calculation is estimating intake rate for each chemical from exposure route. For non-carcinogenic chemicals, the intake rate is calculated by time-averaging the intake over the period of exposure. The result is Chronic Average Daily Dose (CADD) which is used to estimate the hazard quotient by comparing with a safe reference dose. For carcinogenic chemicals, the intake rate is calculated by time-averaging the cumulative dose over a 70 year lifetime. The Lifetime Averaged Daily Dose (LADD) is used to estimate the Incremental Excess Lifetime Cancer Risk (IELCR).

The program developed was used to estimate human health risk for a terrestrial site accidently contaminated with a crude oil spilled from the disrupted oil pipeline (see Fig. 1). As a result of the accident, leaked crude oil penetrated through soil and represented a potential thread of soil, air, groundwater and surface water contamination. An average crude oil concentration in 10-cm soil layer after 3 hours from the accident was 150 g/kg. Concentrations of PHs of concern are shown in Tab. 1. Using the Eco-Risk program, a potential risk for the oil-spill response personnel from the “Priroda-Perm”, Plc. working on the site and preventing oil penetration into the river was calculated (Tab. 2). Model contaminated media were soil and outdoor air. Exposure pathways were ingestion of contaminated soil, dermal contact with soil and inhalation of outdoor air. To calculate contaminant concentrations in air at the receptor point, the Johnson and Ettinger model for soil was used. Estimated values for carcinogenic risk and hazard index were 1.8 x 10^{-4} and 0.4 correspondingly, which did not exceed maximal allowable risk levels ($\leq 10^{-4}$ for carcinogenic and ≤ 1 for non- carcinogenic compounds), thus suggesting the lack of immediate threat for the workers from contaminated soil.

Tab. 1. Oil composition and PH concentrations

PHs	Concentration in soil (mg/kg)
Acenaphthene	2.1
Acenaphthylene	0.3
Antracene	2.1
Benz(a)anthracene	8.7
Benzo(a)pyrene	14.1
Benzo(b)fluoranthene	15.6
Benzo(g,h,i)perylene	14.4
Benzo(k)fluoranthene	17.1
Chrysene	10.5
Dibenz(a,h)anthracene	2.4
Fluoranthene	17.4
Fluorene	0.6
Naphthalene	12.3
Pyrene	18.3
TPH Aliphatic C10-12	1890
TPH Aliphatic C16-35	126900
Total	**128925.9**

Tab. 2. Risk assessment results for oil-spill response workers

PHs	Carcinogenic risk	Hazard index
Acenaphthene	0	1.2e-04
Acenaphthylene	0	0
Antracene	0	2.5E-05
Benz(a)anthracene	8e-06	0
Benzo(a)pyrene	1.3e-04	0
Benzo(b)fluoranthene	1.4e-05	0
Benzo(g,h,i)perylene	0	0
Benzo(k)fluoranthene	1.6e-06	0
Chrysene	9.7e-08	0
Dibenz(a,h)anthracene	2.2e-05	0
Fluoranthene	0	1.5e-03
Fluorene	0	5.3e-05
Naphthalene	0	2.2e-03
Pyrene	0	2.2e-03
TPH Aliphatic C10-12	0	1.7e-01
TPH Aliphatic C16-35	0	2.2e-01
Total	**1.8e-04**	**4.0e-01**

After the site localization, the most suitable remediation method was chosen based on cleanup levels calculated (Fig. 4). Selected bioremediation strategies [10] were tested at pilot scale, including bioaugmentation with hydrocarbon-oxidizing bacterial cultures immobilized onto hydrophobized sawdust and amendment with a biosurfactant for the *ex-situ* site treatment.

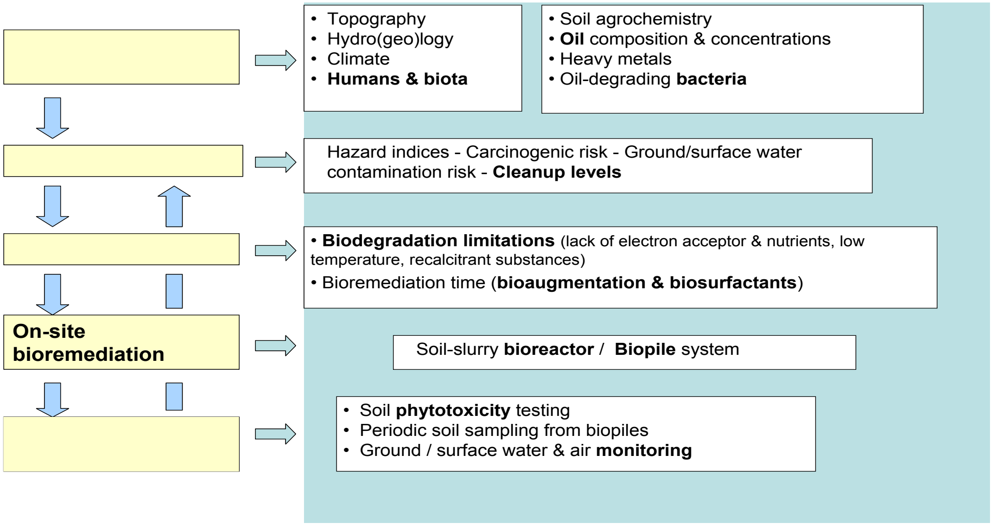


Fig. 4. Flow diagram of risk based management of crude oil-contaminated site.

Two biopiles (5.0 x 3.0 x 0.5 m) were constructed using the crude oil-contaminated soil (Fig. 5). The first biopile received the sawdust-immobilized biocatalyst and *Rhodococcus* biosurfactant, and the second biopile without any addition served as a control. Polyethylene drainage pipes (70 cm length, 8 cm diameter) were placed into the biopiles to improve aeration. Over the course of bioremediation, the biopiles were tilled (after removal of drainage pipes) and watered weekly to maintain soil moisture levels of 20%, and inorganic NPK fertilizer was added. When the air temperature was below 10^{o}C, the cells were covered with a non-woven polymeric fabric covering. The temperature, pH of soil and soil moisture content were monitored weekly. Samples for microbiological and chemical analyses were taken every two weeks. Main agrochemical soil parameters, i.e. pH, soil structure and density, organic carbon, inorganic salts (nitrate, nitrite, phosphate and ammonia), KOI_k and heavy metals were monitored.

Fig. 5. Biopile construction at crude oil-contaminated site.

Results of the field trial after first 3 months of bioremediation confirmed the effectiveness of augmenting a biopile with the sawdust-immobilized biocatalyst and biosurfactant. In this biopile, the oil biodegradation had occurred more rapidly and to a greater extend compared to the control biopile. Removal of TPH aliphatics (C_{10}-C_{30}) representing the major part (90%, w/w) of oil contamination was efficient, reaching 82% for middle-chain (C_{10}-C_{16}) and 63% for long-chain (C_{17}-C_{30}) *n*-alkanes. As a result of biopile treatment, significant reduction (from 90% to 30%) of soil phytotoxicity was obtained thus indicating a great reduction in the ecological risk presented from the soil during bioremediation.

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THE ROLE OF NATURAL ATTENUATION IN THE RISK ANALYSIS FRAMEWORK

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ABSTRACT

Risk assessment is a useful and widely applied tool for the management of contaminated sites, since it provides a rational and objective starting point for priority setting and decision making. Its application in most advanced countries has been prompted by the application of the Risk-Based Corrective Action (RBCA) framework, based on the corresponding ASTM standards. The main strength of the RBCA procedure relies in its capacity of evaluating risks to human health through relatively simple fate and transport and exposure models. However, the experience and the increasing knowledge of the different natural processes taking place in the subsurface, gained over the years, have highlighted some critical issues of the RBCA application to contaminated sites. In particular, it is well known, that the ASTM fate and transport models result in many cases too simplified since they neglect several attenuation processes occurring in the subsurface that several experimental and field studies in the last decades have shown to be particularly relevant. These processes, acting without human intervention, can in fact lead to a significant reduction of the mass, toxicity, mobility, volume and concentrations of contaminants. This paper briefly summarizes the relevance of the different key natural attenuation processes usually taking place in the subsurface and highlights for which contamination scenarios their inclusion as a standard feature for derivation of the site-specific clean up goals could provide a more realistic risk assessment.

INTRODUCTION

The most acknowledged technical and scientific references for the risk-assessment approach are the ASTM Risk-Based Corrective Action (RBCA) standards for evaluating petroleum sites (E 1739-95) and chemical release sites (E 2081-00). The procedure outlined in these documents is based on the information collected during contaminated site investigation to evaluate the potential effects on human health of exposed receptors and on the environment, allowing to assess whether a particular site requires remedial action and eventually the specific risk-based remediation goals. Namely the risk is defined by using site-specific data concerning receptors, exposure potential, site hydrogeology and the type, amount, and toxicity of the chemicals of concern. The ASTM RBCA procedure is based on a "tiered" approach to risk and exposure assessment, where each tier refers to a different level of complexity. In Italy the risk analysis procedure is typically performed using the Tier 2 conditions, that represent a reasonable compromise between the need for a detailed site assessment and the advantage of handling a rather simple and easy-to-use management tool.

The main strength of the Tier 2 RBCA procedure relies in its capacity of evaluating risks to human health through relatively simple fate and transport and exposure models. However, such models are usually too simplified as they neglect several natural attenuation processes occurring in the subsurface. Natural Attenuation refers to naturally-occurring processes in soil and groundwater environments that act without human intervention (U.S.EPA, 1999) and that can be particularly effective in reducing the mass, toxicity, mobility, volume and concentrations of contaminants. These natural processes include biological degradation, volatilization, dispersion, dilution, and sorption of the contaminant onto the organic matter and clay minerals in the soil (Mulligan and Yong, 2004). In the last decades, several studies have demonstrated the occurrence of natural attenuation by studying the attenuation in the unsaturated zone (Lundegard and Johnson 2006; Johnson et al. 2006; Kastanek et al. 1999), the evolution of the plume length (Shih et al. 2004; Newell and Connor, 1998; Prommer et al. 2002, Kao and Prosser, 2001), the mass reduction (Christensen et al. 2000), the geochemical processes (Cozzarelli et al. 2001) and the vertical vapors profiles (Hers et al. 2000; Roggemans et al. 2000; Hohener et al. 2003).

As a results, the application of the ASTM procedure, neglecting almost all the processes described above, can lead in many cases to a significant overestimation of constituent concentrations at the point of exposure (i.e. conservative predictions of constituent migration and attenuation) and consequently of the actual risks.

This paper briefly summarizes the relevance of the different key natural attenuation processes during the vapor intrusion of volatile organic compounds (VOC) from contaminated soil and groundwater into indoor environments the transport and natural attenuation of contaminants in groundwater and the leaching of contaminants to groundwater from dissolved plumes located in the unsaturated zone.

VAPOR INTRUSION INTO INDOOR ENVIRONMENTS

Natural attenuation can significantly influence the potential impact of petroleum hydrocarbon releases, by reducing, mainly through biodegradation processes, the mass, mobility and concentration of contaminants. These processes can be particularly effective in attenuating petroleum hydrocarbon vapors, either from groundwater or unsaturated soil sources. Nevertheless, most risk assessment procedures do not include vapor degradation as a standard feature for developing clean-up levels (e.g. ASTM, 2000). This assumption can lead to an overestimation of the overall human health risk, since vapor intrusion to indoor air is one of the most important exposure pathways at many contaminated sites impacted by volatile compounds (Hers et al., 2003). Consequently the significance of this pathway is the subject of intense debate (Johnson et al., 1998) and in the last years this issue has been the focus of a number of studies. Actually this topic has been addressed since the 1980s, initially with the emphasis placed on assessing impacts of naturally occurring radon intrusion (e.g. Nazaroff et al., 1997; Robinson et al., 1997; Garbesi and Sextro, 1989). In this framework, Johnson and Ettinger (1991) developed an analytical model which is still now the most widely used algorithm for assessing the vapors intrusion to enclosed spaces (Tillman and Weaver, 2006). However several field investigations have shown that the J&E model often overpredicts the indoor concentration of contaminants at sites impacted by petroleum hydrocarbon compounds (Johnson et al., 2002; Provoost et al., 2007). This is especially related to the fact that the J&E algorithm does not include biodegradation, which the field studies have shown to be particularly effective in attenuating vapors (Roggemans et al., 2001; Luo et al., 2009; Lahvis et al., 1999; Dawson and McAlary, 2009).

A range of numerical (e.g. Abreu and Johnson, 2006; Hers et al., 2000; Bozkurt et al., 2009; Yu et al., 2009) and analytical (e.g. Johnson et al.; 1998; DeVaull, 2007; Davis et al. 2009; Parker, 2003; McHugh et al. 2006; Verginelli et al., 2010; Mills et al., 2007) models including aerobic biodegradation were developed to overcome this limitation. These models differ by the underlying assumptions and the conditions at which they can be applied. For instance, some models describe the transient behavior of the vapor intrusion process (e.g. Mills et al., 2007; McHugh et al., 2006), other the spatial variability (Abreu and Johnson, 2006), the non-homogeneous soil conditions (Bozkurt et al., 2009), the oxygen-limited biodegradation (e.g. DeVaull, 2007; Verginelli et al., 2010) or the volatilization from soil contaminated by NAPL (Parker, 2003). All these models account just for the aerobic reaction whereas anaerobic biodegradation is always neglected. However, as reported by Foght (2008) and Haeseler et al. (2010), in the last decades several studies have demonstrated that many aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene (BTEX) and some polycyclic aromatic hydrocarbons (PAHs) can be completely degraded under anaerobic conditions. In fact these experimental and field studies have shown that, under oxygen deficiency, anaerobic bacteria can use nitrate, sulfate, iron, manganese and carbon dioxide as their electron acceptors and break down organic chemicals into smaller compounds even though with usually much slower rates than the aerobic reaction (Schreiber et al., 2004). Besides, anaerobic biodegradation can potentially take place near the vapor source zone where the oxygen concentration may result below the minimum one required to sustain aerobic biodegradation (Boopathy, 2004; Dou et al., 2008; Lee et al., 2001; Johnson et al., 2006; Molins et al., 2010; Bekins et al., 2005; Gray et al., 2010; Salminen et al., 2004). This is somehow confirmed by the frequent methane detection at sites where petroleum hydrocarbons have been released into the subsurface (e.g. Lundegard et al., 2006; Lundegard et al., 2008; Hers et al., 2000), indicative of anaerobic biotransformation under methanogenic conditions (Bekins et al., 2005; Gray et al., 2010).

To assess how anaerobic biodegradation might influence the attenuation of vapors in the sub-soil, a 1-D vapor intrusion model including both aerobic and anaerobic biodegradation was recently developed (Verginelli and Baciocchi, 2011). The model accounts for the different oxygen demand in the subsurface required to sustain the aerobic biodegradation of the compound(s) of concern and for the baseline soil oxygen respiration. In the case of anaerobic reaction under methanogenic conditions, the model accounts for the generation of methane which leads to a further oxygen demand, due to methane oxidation, in the aerobic zone. The model was solved analytically and applied, using representative parameter ranges and values, to identify under which site conditions the attenuation of hydrocarbons migrating into indoor environments is likely to be significant (see Verginelli and Baciocchi, 2011). The obtained results suggest that for many scenarios, aerobic biodegradation is expected to be the main attenuation mechanism, leading to a significant attenuation of vapors concentration with a reduction of the attenuation factor of several orders of magnitude with respect to the Johnson & Ettinger model (J&E). In cases where aerobic biodegradation results limited by the oxygen availability (e.g. for high source concentrations) anaerobic biodegradation may contribute significantly with increased attenuation up to one order of magnitude. The simulations have also shown that the attenuation due to biodegradation is strongly influenced by site-specific conditions (Verginelli and Baciocchi, 2011). The main parameters investigated, which showed a strong influence on transport and consumption of vapors and oxygen in the subsurface, are the biodegradation constants, the source concentration, the cracks fraction of the building, the building area, the building pressure gradient, the source depth and the presence of more biodegradable substances in the subsoil.

EXPOSURE DURATION TO CONTAMINATED GROUNDWATER

Among the different simplifying assumption of Tier 2 ASTM-RBCA models, a key one consists in considering a constant concentration value for the contamination source throughout the entire exposure period of a generic receptor. This approach is somehow mitigated in the case of vapor volatilization from soil, by introducing a limit on the maximum amount of contaminant that can be generated by the contamination source, whereas no mention to this issue is given in the ASTM-RBCA guidelines for contamination source in groundwater, neither for volatilization, nor for migration in the saturated zone. This assumption may lead, for some types of constituents and soils, to extremely conservative results in terms of risk as the source reduction due to the various attenuation processes may occur and have a significant influence on contaminant concentrations (Baciocchi et al. 2010). Recent studies have demonstrated the occurrence of natural attenuation in groundwater by studying the evolution of the plume length (Shih et al. 2004; Newell and Connor, 1998; Prommer et al. 2002) and the mass reduction (Christensen et al. 2000), the geochemical processes (Cozzarelli et al. 2001). Various commercial packages are available for simulating these processes. The analytical models BIOSCREEN (U.S.EPA, 1996) and BIOCHLOR (U.S.EPA, 2000) allow to simulate the NA for petroleum fuel and chlorinated solvents, respectively. The Domenico analytical transport model (Domenico, 1987) is the basis for these models and includes the assumption that the source concentration does not change with time. On the other hand, the RBCA ToolKit (Connor et al. 2007) and the RISC4 (Spence and Walden, 2001) packages account for the decrease in exposure concentration due to volatilization, biodegradation and leaching for contaminated soil and due to dissolution and biodegradation in the case of groundwater source. In addition numerical models such as BIOPLUME III 2-D (Rifai et al. 2000), MODFLOW (Harbaugh et al. 2000) coupled with RT3D (Clement, 1997) and FEFLOW allow to simulate this process.

A model to overcome the limitation of the ASTM-RBCA one, but keeping its original simplicity (Tier 2 framework), was recently developed (Baciocchi et al. 2010). This model (Exposure-Duration Model) accounts for source attenuation, through a simple material balance, identifying the time required for depletion and consequently the effective exposure duration. The only source attenuation mechanism included in this model relies on run-off by groundwater flow, which is assumed to be dominant with respect to volatilization. Although biodegradation may sometimes contribute significantly to source depletion, it is not considered in this model, since it would require a level of characterization, that is usually not available when performing a Tier 2 risk analysis. The results provided by the proposed model were compared with those obtained through the traditional ASTM-RBCA approach, a model based on the source depletion algorithm of the RBCA ToolKit software and a commercial numerical model (FEFLOW), allowing to assess its feasibility for inclusion in risk analysis procedures. The obtained results show that for permeable soil (e.g. Sand) the ASTM-RBCA approach provides more conservative risk values up to two orders of magnitude higher than those obtained applying the Exposure-Duration model. On the contrary the results of the Exposure-Duration model are similar to those provided by the Source-Depletion model and slightly more conservative than those given by the FEFLOW simulations. These results suggest that this modeling approach may represent a simple but meaningful integration of the ASTM-RBCA one, since it keeps its original simplicity, but allows to overcome its limitations in correctly managing risk for specific site conditions

LEACHING OF DISSOLVED PLUMES TO GROUNDWATER

Contamination of soils by petroleum products due to leaking underground storage tanks, accidental spills or improper surface applications is a widespread environmental problem (Karapanagioti et al. 2003). When the volume of spilled product is small, the hydrocarbon may be retained in an immobile condition in the unsaturated zone by capillary forces (Andre et al. 2009). In this case, source zones generating a dissolved-phase, may lead to a long term risk to groundwater since plume in the vadose zone can gradually leach by infiltrating water. Whereas a significant volume spill of Nonaqueous Phase Liquids (DNAPL or LNAPL) may take hours to days to reach a water table, a dissolved plume leached from a shallow source may require years to decades (Rivett et al. 2011). In this time framework if natural attenuation processes are significant, leached plumes may never reach groundwater, or else be substantially delayed with reduced concentrations (Rivett et al. 2011). As a matter of fact, in the last decades several studies have demonstrated the occurrence of natural attenuation in the unsaturated zone (Lundegard and Johnson 2006; Johnson et al. 2006; Kastanek et al. 1999; Hers et al. 2000; Roggemans et al. 2000). Hence, accounting for these processes is a crucial issue in order to properly assess the risk for groundwater contamination from point sources (Troldborg et al. 2009). However, in most screening tools for risk assessment, the description of transport through the unsaturated zone is very simplified. For instance, the leachate ASTM model (ASTM, 2000) accounts just for dissolution of contaminants into infiltrating water and dilution within the underlying groundwater, whereas no attenuation pathways are considered. These assumptions may lead in some cases to an overestimation of the concentrations expected in the underlying aquifer.

In this view, in order to evaluate the expected significance of the different attenuation pathways, an analytical model accounting for the transport and attenuation by multiple mechanisms in the unsaturated zone and in the source, was very recently developed and applied (Verginelli and Baciocchi, 2013). Namely, this model accounts for the key processes affecting the contaminants leaching scenario such as advection due to infiltrating water, dispersion and diffusion, sorption, first-order degradation in the water phase and source depletion due to biodegradation and dissolution. The model was solved analytically and applied, using representative parameter ranges and values, to identify the dependence and the expected relevance of natural attenuation and depletion timeframes on soil conditions, site geometry and compounds properties (see Verginelli and Baciocchi, 2013).

The obtained results suggest that BTEX are likely to be attenuated in the source due to their ready biodegradation (assuming biodegradation constant rates in the order of 0.01 - 1 d^{-1}) and mobility, whereas a minor relevance of the attenuation is expected to occur during transport, as these compounds generally migrate quite rapidly and consequently the time available for biodegradation to take place before reaching the aquifer is generally low. On the contrary, heavier compounds such as PAHs, that are more persistent in the vadose zone, can be attenuated during transport since the residence time in the subsurface can reach in some cases up to thousands of years. In this time framework, even with relatively slow biodegradation (e.g. in the order of 0.0001 – 0.001 d^{-1}), attenuation can result significant. These results suggest that the ASTM model used in the risk assessment procedure, which neglects both these processes, can lead to an overall overestimation of the concentration reaching the groundwater and consequently of the risk calculated for the downstream receptor.

CONCLUSIONS

The main strength of the RBCA procedure relies in its capacity of evaluating risks to human health through relatively simple fate and transport and exposure models. However, such models are usually based on very simplified assumptions which can lead, together with the use of “reasonably worst case” exposure scenarios, to unreasonably low clean-up goals, thus making the whole remediation economically unsustainable. Among these, a key one consists in neglecting natural attenuation processes taking place in the subsurface. Several experimental and field studies in the last decades have shown that these processes are particularly relevant, acting without human intervention and can in fact lead to a significant reduction of the mass, toxicity, mobility, volume and concentrations of contaminants, that are not accounted for in the RBCA risk procedure.

In this view, several approaches were proposed in order to integrate the results of RBCA – ASTM risk assessment in order to properly take into account the site-specific processes influencing the fate and transport of contaminants at a site.

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A NEW SOFTWARE (RISK-NET) FOR THE APPLICATION OF RISK ASSESSMENT TO CONTAMINATED SITES

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KEYWORDS
Contaminated Sites, Risk assessment, RBCA procedure, Free Tool

ABSTRACT

In this work a new software (Risk-net), designed to complete all calculations required for the Tier 1 and Tier 2 ASTM-RBCA planning process, is presented. Risk-net was developed by the Department of Civil Engineering of the University of Rome "Tor Vergata" and validated by the Italian Network on the Management and Remediation of Contaminated Sites (Reconnet). The software allows to apply the risk assessment procedure both in forward and backward mode, thus evaluating the risks or the clean-up levels for a contaminated site, respectively. The program uses a simple and user-friendly graphical interface through which the user can simply define the different input parameters. To accelerate the compiling process, according to the conceptual model defined by the user, only the data actually used in the calculation are required. Some controls also allow to manage the presence of conceptual and numerical errors. The results are returned in terms of risk (for human health and groundwater resources) and clean-up levels. Intermediate outputs are also displayed allowing the user, to evaluate more critically the obtained results. The main features of Risk-net concern the possibility to use the program to perform analysis for the evaluation of the mobility of free product in the subsoil, the identification and visualization of contaminants distribution in the different phases of the soil (saturated and unsaturated), the presence of different receptors within (on-site) or near the site (off-site), the temporal and spatial evolution of the contamination in the aquifer and the calculation of clean-up levels for hydrocarbons (C <12, C> 12 and Total Hydrocarbons) as a function of the different classes MADEP identified by the user.
Risk-net is a freeware software which can be downloaded from the website of the Reconnet network: www.reconnet.net.

INTRODUCTION

In the last decades soil and groundwater contamination caused by abandoned waste disposal sites and industrial activities has become a key environmental issue in most of advanced countries. Risks for human health, as a result of toxic chemicals introduced into the environment, are in fact a matter of main concern to modern society and the effective management of environmental contamination problems has become an important environmental priority of both national and European policies (Kofi Asante-Duah, 1998). In this framework, the management of contaminated sites often relies on a risk-based corrective action (RBCA) approach, where the actual pollution of the site is evaluated depending on the effective risk posed to the human health or environment. For instance, this is the case of the Italian regulatory approach, where the guidelines for risk assessment application developed by the national environmental agency (ISPRA) are based on the ASTM RBCA procedure. The ASTM RBCA is based on a three-tiered approach to risk and exposure assessment, where each tier refers to a different level of complexity. Namely in the RBCA Tier 1, aimed to the definition of the contamination screening values, only on-site receptors are considered. Transport of contaminants is described through simple analytical models and conservative default values are used for all hydro-geological, geometrical and exposure data, without requiring any site characterization. In Tier 2, aimed to evaluate site-specific target levels, off-site receptors are included in the conceptual model, all input data should possibly be site-specific, whereas models used to describe contaminants' transport are still analytical. Usually, the risk analysis procedure is performed using the Tier 2 conditions, that represent a reasonable compromise between the need for a detailed site assessment and the advantage of handling a rather simple and easy-to-use management tool (Baciocchi et al. 2010). Therefore, only in very specific situations, where a more detailed description of the contaminant transport through numerical models is required, risk analysis is performed following the Tier 3 approach (Verginelli and Baciocchi 2013).
For the calculation of the Tier 1 and Tier 2 RBCA several software packages are available. The most commonly used in Italy, which have been validated in the ISPRA guidelines (2008), are: RBCA Tool Kit, BP-RISC and Giuditta. However, as highlighted in the ISPRA document (2008), these softwares do not allow the full implementation of the risk analysis procedure defined in these guidelines and by the Italian law.
In this work a new software (called Risk-net), designed to complete all calculations required for the ISPRA (2008) planning process, is presented.

Risk-net was developed by the Department of Civil Engineering of the University of Rome "Tor Vergata" and validated by the Reconnet network. The software is available for free on the website of the Reconnet network: www.reconnet.net.

DESCRIPTION OF THE DEVELOPED SOFTWARE

The Risk-net software has been developed within the Reconnet network by the Department of Civil Engineering of the University of Rome “Tor Vergata”, with the aim of providing a tool based on the ISPRA National guidelines for risk analysis application to contaminated sites.

The software allows to apply the risk assessment procedure both in forward and backward mode, thus evaluating the risks or the clean-up levels for a contaminated site, respectively.

Namely for each exposure pathway activated by the user, Risk-net calculates, through the Fate and Transport (F&T) models described in the ISPRA guidelines (2008), the maximum steady-state concentrations expected at the point of exposure. Afterward, on the basis of exposure parameters defined by the user, the daily dose assumed by each receptor considered is calculated. These doses combined with the corresponding toxicological parameters are used for the calculation of risk and clean-up levels (CSR) for each contaminant and active route. Finally the effects related to the presence of multiple routes of exposure and multi-component contamination is calculated.

The key features of Risk-net include:

- Baseline Risks and Risk-Based Clean-up Level Calculations: Risk-net was designed to complete the calculations required for Tier 1 and Tier 2 RBCA evaluations according to the ISPRA Italian guidelines for risk analysis application to contaminated sites.
- Fate and Transport Models: simple analytical models for air, groundwater and soil exposure pathways, including all models used in the ISPRA (2008) standard.
- Chemical and Toxicological Database: Pre-loaded toxicological and chemical parameter library (ISS-ISPESL Database). The database is customizable by the user.
- User-Friendly Interface: User-friendly graphical interface with on-line help, unit conversion and Load/Save capability.

MAIN SCREEN

The main screen is automatically opened at startup (Fig. 1). On this screen the user can enter the project information (e.g. Site Location, Date, Compiled By) select the type of analysis and risk-based calculations to be performed (i.e. Forward or Backward mode) and progressively access to the different input and output screens.

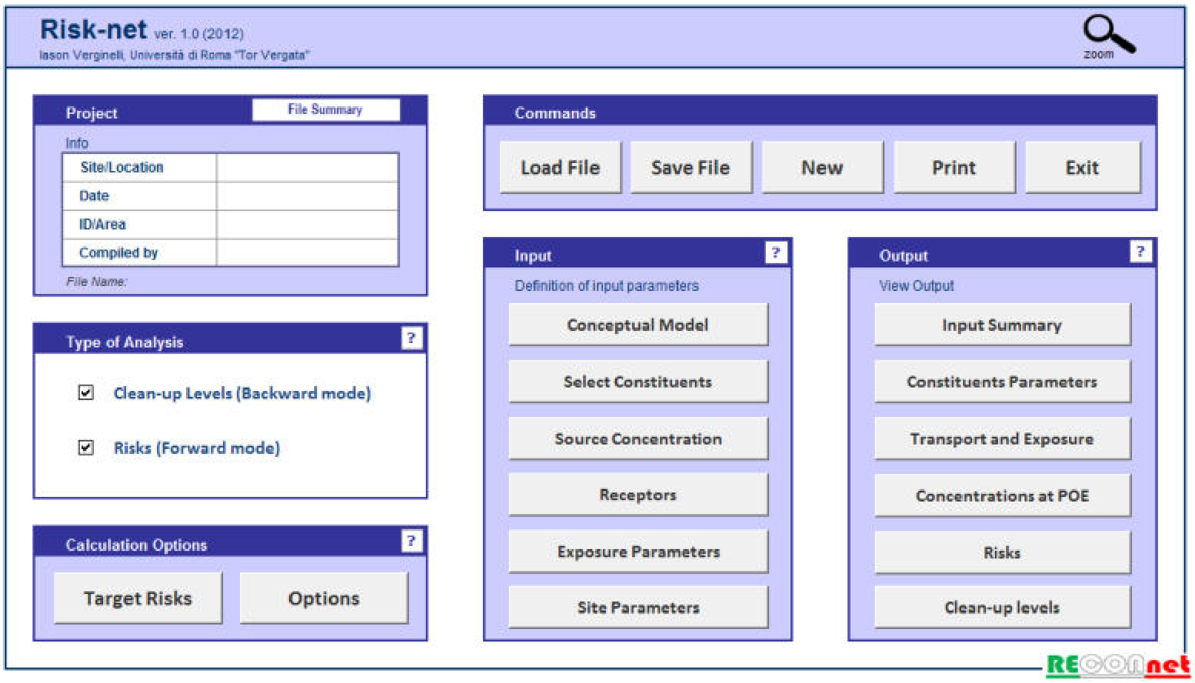


Fig. 1. Main Screen of Risk-net.**INPUT**

This section reports a brief summary of the main features of the Risk-net software.

Exposure Pathways. In Risk-net the following exposure pathways can be activated:

Surface Soil

- Dermal contact
- Soil ingestion
- Outdoor air inhalation
- Indoor air inhalation
- Outdoor particulate inhalation
- Indoor particulate inhalation
- Leaching to groundwater

Subsurface Soil

- Outdoor air inhalation
- Indoor air inhalation
- Leaching to groundwater

Groundwater

- Outdoor vapor inhalation
- Indoor vapor inhalation
- Affected groundwater

Moreover the user can specify if the exposure occurs on-site (receptor located at the source zone) or off-site (receptor at any point away from the source zone).

Receptors. After defining potential source media, transport models and exposure pathways, the user can select the types of soil use and the receptors. Namely the types of soil use and receptors are differentiated into:

Residential or Recreational use

- Child: Children (default age 6), with a low body weight.
- Adult: Adult with a full grown body weight.
- Adjusted (Child + Adult): For the residential exposure scenario, the “Adjusted” option calculates an average exposure values among the child and adult. Age adjustment is applied for carcinogenic contaminants only, where carcinogenic exposures are assumed to be chronic over the lifetime of the receptor.

Commercial or Industrial use

- Adult: Adult working at a full-time job.

Chemicals of concern. The Risk-net software includes a Chemical Toxicity database pre-loaded with the Database of ISS-ISPESL (2009). The chemicals of concern may be chosen from this database or new chemicals may be added or modified to the database and then chosen as a chemical of concern. The values modified by the user change color to red and the chemical name is indicated with an asterisk.

Source Concentration. If baseline risks are to be calculated, the user must define the representative concentrations in the source of the different chemicals of concern. Namely the user can define, for each chemicals of concern, the total concentration in soil (or in groundwater) or specify the soil gas concentration as the source term. In addition, in the case of hydrocarbons contamination, the user can enter the concentration values for the different hydrocarbons fractions. Namely the user can choose between the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) and the Massachusetts Department of Environmental Protection (MADEP) classification. The software calculates the total concentration for C>12 and C<12 macro fractions.

Exposure Parameters. On this screen, the user must define the exposure factors for each complete pathway. Initially, this section contains the default values corresponding to ISPRA guidelines (2008). There are different exposure factor columns representing the different types of receptors that can be modeled with the software. These receptor types allow the user to calculate the baseline risks and the cleanup levels based on different physical (e.g., skin area, body weight, etc.) and exposure-related (e.g., soil ingestion rate, inhalation rate, etc.) parameters.

Site-Specific Parameters. In this section the user can define the site-specific parameters required for the application of the fate and transport models selected. Initially, this section contains the default values corresponding to ISPRA guidelines (2008).
Namely the user must enter the following parameters:

- Vadose zone: source and soil geometry, soil properties, rainfall infiltration rate, fraction of organic carbon, pH, etc.
- Groundwater zone: source and groundwater geometry, physical characteristics, fraction of organic carbon and other transport properties.
- Outdoor air zone: source geometry, wind speed, dispersion in air, particulate emissions, etc.
- Indoor air zone: building geometry and properties, air exchange rate, indoor/outdoor differential pressure, etc.

OUTPUT

This section reports a brief summary of the main output provided by Risk-net.

Input Parameters Summary. In this screen a summary of all input parameters and option calculation used in the software is reported. The values modified by the user are highlighted. In addition the software shows the parameters not required for the specific calculation.

Exposure Pathway Flowchart. The Exposure pathway flowchart shows all selected source media, transport mechanisms, exposure media and receptors. This screen allows the user to check the problem setup and, if necessary, revise the exposure pathway selections.

Chemical and toxicological data for the selected contaminants. This output screen reports the chemical and toxicological data used for the selected contaminants. The values modified by the user are highlighted.

Fate & Transport models. the software reports the fate and transport (F&T) factors calculated for the selected contaminants.

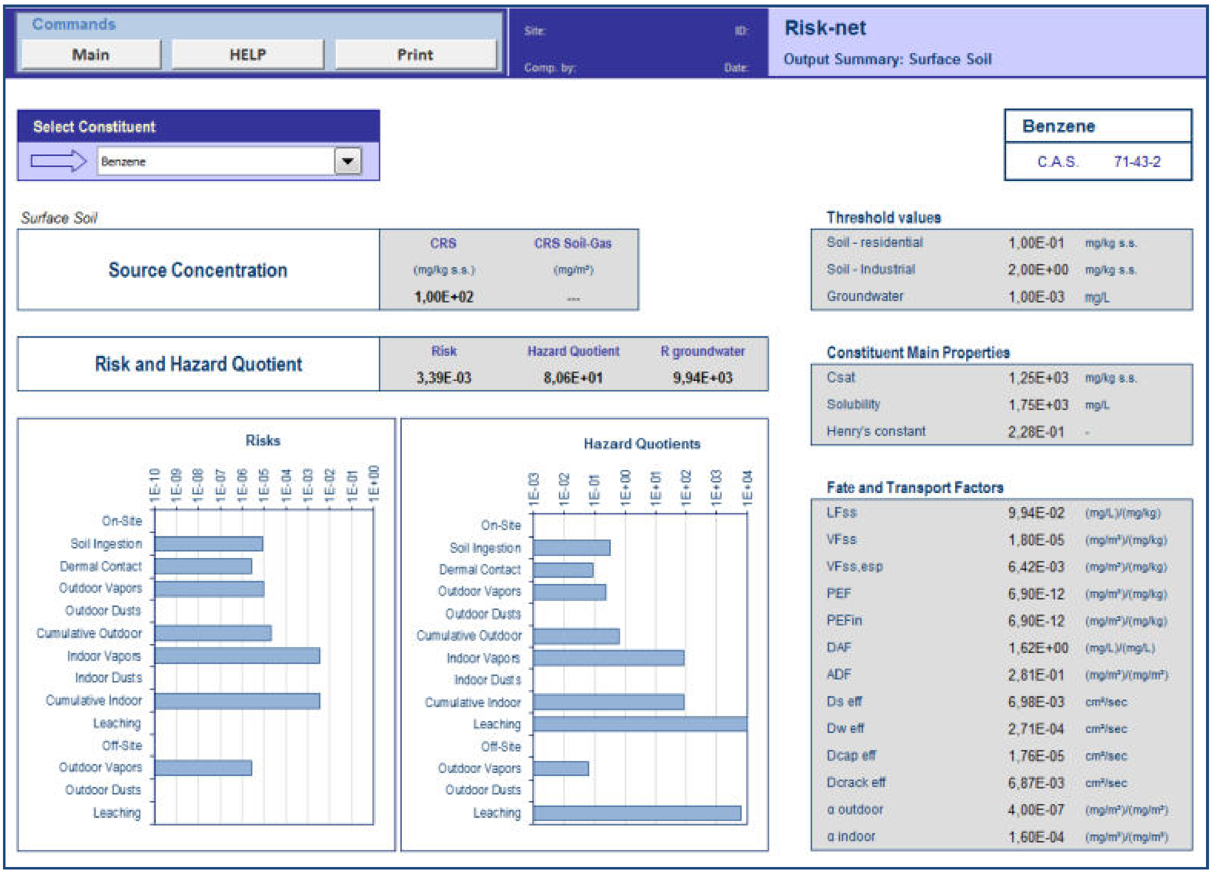
Partition behavior of the selected contaminants. In this screen the user can assess the different partition behavior of the selected contaminants. This screen also reports the different concentrations at the point of exposure (Cpoe) that are also calculated.

Intake Rates. This screen reports the intake rates calculated for the different exposure pathways for each receptor activated by the user.

Transient Domenico Analysis. In this screen the user can evaluate the transient groundwater modeling results for the different selected contaminants. This evaluation is not used for the risk and clean up levels calculation but can be useful for a risk management decision for example to assess when an exposure limit might be exceeded.

Green Ampt Analysis. In this screen the user can evaluate the leaching modeling results with the Green & Ampt (1911) equation for the different contaminants selected. This evaluation is not used for the risk and clean up levels calculation but can be useful for a risk management decision for example to assess the leaching velocity and the expected role of biodegradation in attenuating the selected contaminant.

Baseline Risk. For each media of interest (surface soils, subsurface soils and groundwater) the software reports the baseline risk calculations for each complete exposure pathway (outdoor air, indoor air, soil, etc) and the associated receptors (on-site or off-site). Namely the software calculate the human health risks associated with exposure to the contaminant on the basis of average daily intake rates and the corresponding toxicological parameters for carcinogenic and non-carcinogenic effects. In addition the software calculates the risk for the groundwater resource (R_{gw}) by comparing the groundwater concentrations calculated at the point of compliance (POC) with the values defined by the Italian law (CSC). For each complete pathway, the software provides both individual and additive constituent results for carcinogens (R) and non-carcinogens (HI).
Besides the user can also visualize for each individual contaminant a summary of the different risks calculated and of the different fate and transport factors used for their derivation.



Risk-net

Output Summary: Surface Soil

Select Constituent: Benzene

Benzene

C.A.S. 71-43-2

Surface Soil

	CRS (mg/kg s.s.)	CRS Soil-Gas (mg/m³)
Source Concentration	1,00E+02	---

	Risk	Hazard Quotient	R groundwater
Risk and Hazard Quotient	3,39E-03	8,06E+01	9,94E+03

Threshold values

Soil - residential	1,00E-01	mg/kg s.s.
Soil - Industrial	2,00E+00	mg/kg s.s.
Groundwater	1,00E-03	mg/L

Constituent Main Properties

Csat	1,25E+03	mg/kg s.s.
Solubility	1,75E+03	mg/L
Henry's constant	2,28E-01	-

Fate and Transport Factors

LFss	9,94E-02	(mg/L)/(mg/kg)
VFss	1,80E-05	(mg/m³)/(mg/kg)
VFss,esp	6,42E-03	(mg/m³)/(mg/kg)
PEF	6,90E-12	(mg/m³)/(mg/kg)
PEFin	6,90E-12	(mg/m³)/(mg/kg)
DAF	1,62E+00	(mg/L)/(mg/L)
ADF	2,81E-01	(mg/m³)/(mg/m³)
Ds eff	6,98E-03	cm²/sec
Dw eff	2,71E-04	cm²/sec
Dcap eff	1,76E-05	cm²/sec
Dcrack eff	6,87E-03	cm²/sec
α outdoor	4,00E-07	(mg/m³)/(mg/m³)
α indoor	1,60E-04	(mg/m³)/(mg/m³)

Fig. 2. Example of an output screen provided by Risk-net.

Free-phase Liquid Migration. In the case of source concentrations greater than the saturation ones (Csat) the software can be used to evaluate if the NAPL (non-aqueous phase liquid) detected in the soil is expected to be mobile. In fact as reported by the ASTM standard (2000) a NAPL may be present in soil, but immobile. The mobility of a NAPL is not governed by thermodynamic properties but by capillary, viscous and gravity forces acting on the bulk NAPL phase. To assess this aspect, the software uses the simple screening model reported in the ASTM standard allowing to calculate for each contaminant (liquid at standard conditions of temperature and pressure) a screening concentration above which the NAPL is expected to become mobile.

Clean-up Levels. For each media of interest (surface soils, subsurface soils and groundwater) the software reports the calculated clean-up levels for the different selected contaminants. Moreover, in order to compute clean-up levels based on cumulative risk effects, the software allows the user to adjust the individual constituent target levels calculated to meet the cumulative risk goals. Thus the clean-up levels calculated represent the maximum acceptable concentration in the affected source medium (soil or groundwater) that is protective of a human or groundwater receptor located at a relevant point of exposure (POE). In the case of hydrocarbons contamination, the software also calculates, according to the Italian law (D.Lgs 152/06 and D.Lgs 04/08), the clean-up levels for the C>12 and C<12 macro fractions. Afterwards the user can also visualize for each individual contaminant a summary of the clean-up levels calculated and the different fate and transport factors used for their derivation.

CONCLUSIONS

For the calculation of the RBCA procedure several software packages are available. The most commonly used in Italy, which have been validated in the ISPRA guidelines (2008), are the RBCA Tool Kit, the BP-RISC and Giuditta. However, as highlighted in the ISPRA document (2008), such tools do not allow the full implementation of the risk analysis procedure defined in these guidelines according to the Italian law.
In this work a new software (called Risk-net), designed to complete all calculations required for the ISPRA (2008) planning process, was presented. Risk-net was developed by the Department of Civil Engineering of the

University of Rome "Tor Vergata" and validated by the Reconnet network. The software allows to apply the risk assessment procedure both in forward and backward mode, thus evaluating the risk or the clean-up objective for a contaminated site, respectively.

The program uses a simple and user-friendly graphical interface through which the user can simply define the different input parameters. To accelerate the compiling process, according to the conceptual model defined by the user, only the data actually used in the calculation are required. Some controls also allow to manage the presence of conceptual and numerical errors. The results are returned in terms of risk (for human health and groundwater resources) and clean-up levels (Threshold Risk Concentrations, CSR). Intermediate outputs are also displayed allowing the user, to evaluate more critically the obtained results. The main features of Risk-net concern the possibility to use the program to perform analysis for the evaluation of the mobility of free product in the subsoil, the identification and visualization of contaminants distribution in the different phases of the soil (saturated and unsaturated), the presence of different receptors within (on-site) or near the site (off-site), the temporal and spatial evolution of the contamination in the aquifer and the calculation of clean-up levels for hydrocarbons (Hydrocarbons C <12, Hydrocarbon C> 12 and Total Hydrocarbons) as a function of the different classes MADEP identified by the user.

The software can be downloaded for free from the website of the Reconnet network: www.reconnet.net.

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ECOLOGICAL RISK ASSESSMENT FOR SOILS CONTAMINATED WITH PAHS – TREATS TO SOIL HABITAT FUNCTION

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KEYWORDS
Ecological risk assessment, habitat function, lines of evidence, PAHs, soil contamination

ABSTRACT

Soil is a sink for a wide range of anthropogenic hazardous contaminants, including PAHs. Once deposited to surface soils, PAHs often persist for many years and can generate direct and indirect risk for soil functions (e.g. habitat, retention). The high level of pollutants may cause an adverse effect on soil organisms and decrease soil biodiversity and quality (Maliszewska-Kordybach et al., 2009). For assessing the risk from chemical contamination the ecological risk assessment (ERA) methods are applied.

Ecological risk assessment is a process for collecting, organizing, and analyzing information to estimate the likelihood of undesired effects on nonhuman organisms, populations, or ecosystems. In practice ERA process is performed in phases or tiers, including scoping assessment, screening assessment, and definitive baseline assessment (Sutter II et al., 2000; Jensen and Mesman, 2007). Scoping assessments determine whether an ecological risk assessment is needed; screening assessments determine what contaminants, media, and receptors need to be assessed; and definitive assessments determine the nature and magnitude of risks (Sutter II et al., 2000). Each tiers of risk assessments should include three phases: problem formulation, analysis and risk characterization. The first phase includes the assessment of the purposes and the methods of investigation. The second phase is focused on the evaluation of the paths of exposure to stressors and the relationships between the stressors and ecological effects. In the third phase the exposure and stressor-response profiles are integrated through the risk estimation process (US EPA, 1998; Tarazona and Vega, 2002; Jensen and Mesman, 2007).

The aim of the studies was to evaluate the area contaminated with PAHs using ERA - Triad procedure based on the analysis of three different Lines of Evidence - LoEs (chemical, ecotoxicological and ecological). The first two tiers (simple and refined screening) of ERA procedure were performed.

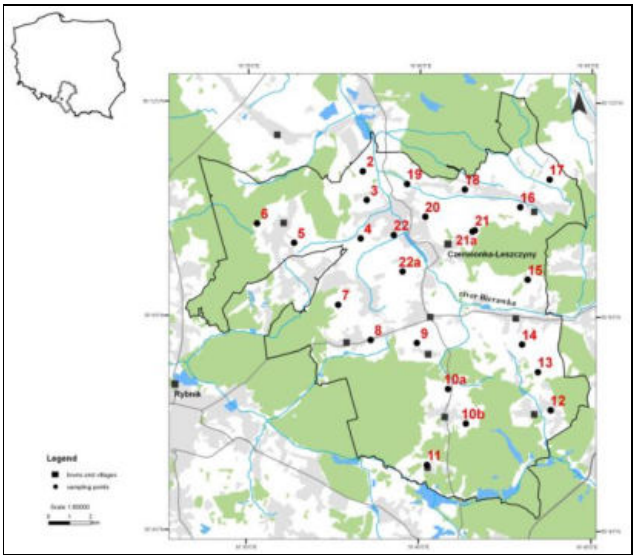

Fig. 1. Location of sampling points in the research area

The Triad is a weight of evidence approach (WoE) originally developed in order to evaluate sediment quality (Long and Chapman, 1985). However, this procedure recently is recommended by the EU project Liberation for the site-specific risk assessment (Jensen and Mesman, 2007) and is included in legislation and standardization process (ISO/TC 190 Soil Quality). The Triad approach gives a good opportunity to assess possible irregularities in the ecosystem functioning and usually is performed in few different tiers (Jensen and Mesman, 2007). In each tier, an assessment is performed with generally two possible outcomes: either a judgment of the absence of unacceptable risks can be given, and the total assessment is finished, or unacceptable risks can be excluded and the assessment has to be followed into the next tier. A tiered approach often starts with a generic Risk Assessment, that is, comparing measured value with Soil Quality Standards (Swartjes 2011).

The study area covered the territory of about 100 km^2 in the Upper Silesia region in Poland (Fig. 1). Soil samples were collected from the surface layer (0 – 30 cm) of agricultural land surrounding coking plant with 100 years of production history. Additionally, the asphalt production and coal mining were identified as the possible emission/contamination sources. The first step of the Triad comprised preliminary site assessment including topographic and land use description and soils characteristic (physicochemical properties, content of contaminants: heavy metals and PAHs) – Tab. 1.

Tab. 1. Statictical evaluation of selected soil properties (n=24)

	range	median	AVG	SD	LQ	UQ	CoV (%)
fr <0,002 (%)	1-11	2	3	3	1	3,5	100
fr <0,02 (%)	7-32	18	18	7	13	21	37
OM (%)	1,6-10,1	3,0	3,7	2,3	2,4	3,3	61
pH_{KCl}	3,7-6,8	5,3	5,1	0,8	4,4	5,5	17
Zn^a	13-886	48	87	172	36	77	197
Pb^a	13-353	35	46	66	26	38	143
Σ 9 PAH^a	0,2-3,9	0,9	1,2	1,0	0,5	1,5	86
BaP^a	0,02-0,44	0,08	0,13	0,11	0,05	0,15	91

^{a}/ content of metals or PAHs in mg kg^{-1}; OM – organic matter content, Σ 9 PAH – hydrocarbons included in Polish regulations (Dz.U.02.165.1359, 2002), AVG – average value, SD - standard deviation, LQ – lower quartile, UQ – upper quartile, CoV – variation coefficient.

The first screening stage of ERA was based on the comparison of soil PAHs concentrations in the sampling points with the Polish soil guidelines (Dz. U. 02.165.1359, 2002) for soils of an agricultural use (a threshold value of 1 mg Σ9PAH kg^{-1}). Application of this criterion allowed to calculate the hazard quotient (HQ 0,27 – 4,01). The results indicated that potential negative effects towards the ecological receptors may be expected at 46% of the area (9 sampling points) - Fig. 2.

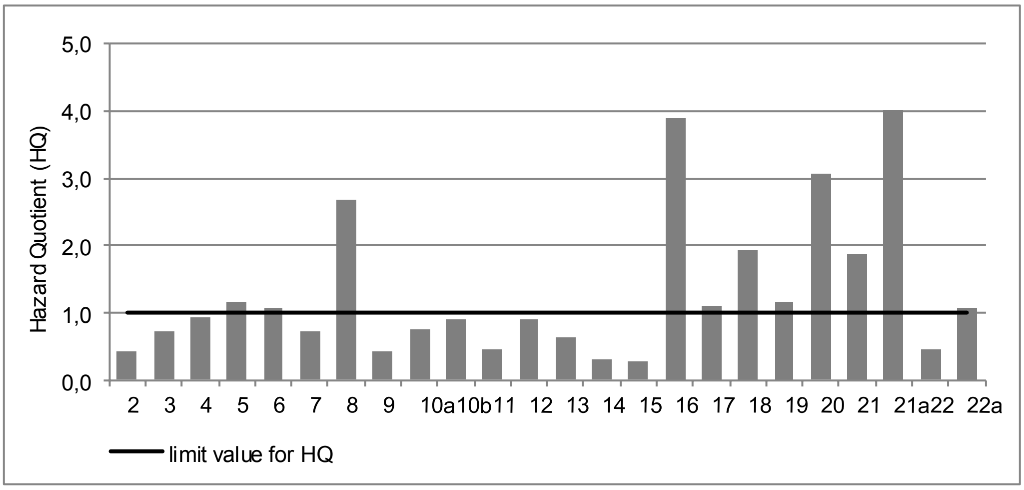

Fig. 2. Hazard quotient values; comparison of environmental 9PAHs concentrations with the limit value according Polish regulation (Dz. U. 02.165.1359, 2002).

These points delineated area of high risk where the risk assessment procedure is really needed (included in the further ERA stages).

The next tier of ERA (refined screening) embraced three LoEs (chemical, ecotoxicological and ecological). Chemical line was based on the determinations of PAHs content in soil samples (as in the previous tier). Ecotoxicological line was covered by the results of the Toxi-screeing microbiotest based on the luminescent bacteria (*Vibrio fischeri*) activity while ecological indices comprised microbial parameters related to respiration. The risk factors for each sampling point and each line of evidence were calculated according to the method described by Jensen and Mesman (2007). Risk values were expressed in an effect scale ranging from zero (no effect) to one (maximum effect) with samples value related to the reference soil (zero value). For each sampling point the calculation of the risk factors included three steps: scaling of results within individual LoE, integrating the information from LoEs and calculation the integrated risk factor (IR).

Tab. 2. Risk factors for individual Lines of Evidence and integrated risk for sites included in Tier 2 (refined screening).

Tier 2	**Sampling sites**								
	8	**16**	**17**	**18**	**19**	**20**	**21**	**21a**	**22a**
Chem-LoE	0,60	0,70	0,31	0,51	0,33	0,65	0,50	0,71	0,31
Ecotox-LoE	0,09	0,16	0,14	0,68	0,20	0,63	0,22	0,20	0,21
Ecol-LoE	0,33	0,01	0,01	0,71	0,01	0,07	0,01	0,36	0,01
IR	**0,38**	**0,37**	**0,16**	**0,64**	**0,19**	**0,51**	**0,24**	**0,47**	**0,18**

Chem-LoE chemical line of evidence (based on 9PAHs content), Ecotox-LoE ecotoxicological line of evidence (based on the *V.fischeri* activity), Ecol-LoE ecological line of evidence (based on substrate induced respiration), IR Integrated Risk values – marked in grey values above the limit of acceptable risk (0,25) for agricultural land-use according to Niemeyer et al. (2008).

The calculated chemical LoE risk values were in the range of 0,31 – 0,71 and were mostly higher than the ecotoxicological and ecological LoE risk factors (Tab. 2). Integrated risk factors values ranged from 0,16 to 0,64. In four cases, the IR were less than 0,25, indicating that there is no risk – as it is recommendend by Niemeyer et al. (2008). These points were distributed at a significant distance from the emission sources of PAHs - coking plant and power plant. For other soils (8, 16, 18, 20, 21a) the high values of IR were found, which indicates the possibility for adverse environmental effects. The points with IR > 0,25 were selected for the next tier of the ERA procedure (detailed assessment).

Calculation of integrated risk indexes led to delineate the limited area of possible high ecological risk to soil habitat function. The area of the high risk should be excluded from agricultural use and/or remediated.

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OBSOLETE PESTICIDES TECHNICAL STUDY AND CONTAMINATED SITE REMEDIATION IN THE REPUBLIC OF UZBEKISTAN

Ms.Zulfiya Artikova - Mr. Zokir Rahimov

Republic of Uzbekistan is located in Central Asia. Cotton growing still remains the major agricultural sector, and the Republic ranks second in the world as regards the exportation of cotton.
Chemical means of protection from pests, diseases and weeds are widely used in agricultural production.

Obsolete and unusable stocks of pesticides remain a global environmental problem. Their accumulation is a direct result of many years of negligence in pesticides handling.
The older pesticides (since 1972) have been kept in special underground burials, which are made concrete-type and located far off the residential areas. There are 13 such burials in Uzbekistan, most of which are filled with pesticides, insecticides, containers for thereof, industrial wastes, and covered with slabs and soil. Total area of facilities is more 60 hectares.

The State Committee for Nature Protection of the Republic of Uzbekistan implements state control and interdepartmental regulation in the area of environmental protection. The State Environmental Monitoring adopted by the Government of the Republic includes a list of priority sources of contamination, and areas around pesticides warehouses, burials and agricultural airdromes.
The problem of hazardous waste treatment is not easy. It is technically difficult, dangerous and resource intensive. Such work should be performed by experts with a necessary experience and training in obsolete pesticide stocks management.

At the initiative of the World Bank (WB) Obsolete Pesticides Technical Study in the Kyrgyz Republic, the Republic of Tajikistan and the Republic of Uzbekistan started in 2009. The project was implemented by a Consortium of TAUW (Tauw BV), Milieukontakt International, International HCH & Pesticides Association (IHPA), Witteveen and Bos and Green Cross Switzerland. One of priority of the project team was studied Yangiaryk burial site in Khorezm region of the Republic of Uzbekistan.
An inventory of the burial site was carried out jointly with specialists of the State Committee for Nature Protection and representatives of the regional inspectorates of analytical control of the country. They completed ten days training module on safe handling of hazardous stockpiles of obsolete pesticides and risk assessments for humans and the environment from exposure to such stockpiles.
During the inventory soil samples from the most contaminated parts were taken, as well as water samples from the collector and ground water for organochlorine pesticides analysis. A portable well was installed in the most low-lying part of the burial site for taking ground water samples.
Organochlorine pesticides such as DDT, DDD, DDE and HCH in amounts far exceeding the maximum allowable concentrations were found in the groundwater samples. Also, high concentrations of DDT were detected in water samples taken from the collector reservoir near the burial site.

The study of Yangiaryk site included standard parameters of risk assessment, which were used for design and description of a conceptual model of the site. Yangiaryk burial site is located on sandy soil in desert area. The access is limited, but the perimeter is unfenced. Containments, in which the substances were buried, are partially damaged. Direct contact with the waste is possible, however, the dumpsite is quite far from the village. Precipitations and erosion processes might facilitate contamination of various environmental sites.

Risk assessment focuses on pollution impact analysis, including direct contact of human beings with a source of pollution, as well as direct contact of people with contaminated soil, of cattle and wild animals with surface waters, including an indicative assessment of the risks to the ecosystem as a whole.

Based on these assessments, a significant impact on the ecosystem can not be excluded since the concentration of harmful substances in the soil exceeds the maximum allowable concentration.

Yangiaryk burial site is concerned, there is a need for urgent action to enhance the environmental condition and the experts propose specific short-term, medium-term and long-term activities for mitigation and elimination of acute, potential and latent risks.

To restore the heavily polluted soil layer it is proposed to remove the soil and deliver it to the central site, where the soil may be biologically treated in specially designed pits. The remaining contaminated soil can be treated on-site using bio- and phytoremediation, described in the report by the experts.

Scientists of the Academy of Sciences of the Republic of Uzbekistan possess certain experience in remediation of soils contaminated with organochlorine pesticides by microbial destruction. Bacterial strains that are actively destroying the HCH (hexachlorocyclohexane) and PCBs (polychlorinated biphenyls) were isolated.

A research and coordination diagnostic center "Healthy Soil" was established under the Institute of Microbiology of the Academy of Sciences. The Center specialists diagnose soils, using modern research methods – microbiological, botanical and biochemical. They develop evidence-based and tested recommendations for improvement of soil and fertilizer application, combining conventional farming techniques with biological methods, which results in environmentally friendly products.

INVENTORY OF POP PESTICIDES POLLUTED AREAS IN MOLDOVA

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

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 base on a unified questionnaire; 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 effectively storing, 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.mediu.gov.md. The information on POPs polluted sites is to be periodically updated by 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.

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 important – 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:

- 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).

1. 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 the country undergone 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 a small minority has previously been described and assessed in terms of health and environmental risks. Moreover, most existing data were inaccessible or unusable because scattered between different institutions (or different levels of the same institution) and existed 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 for identifying the potentially contaminated sites it was decided to gather information at the local level rather then to use data available at the central level. Information was basically collected from two sources: the mayoralties and local operators. Official letters were sent to all rural and urban mayoralties (898 in total) asking to indicate on map the location of former facilities related to pesticides use. In parallel, have been hired local operators with relevant knowledge and professional experience to complete the task.

The information collected from the mayoralties 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 developed standard procedures in order to assure the quality and completeness of work done. The information obtained was processed and incorporated in the database.

The general approach to assessing the hazards associated with the sites potentially contaminated with obsolete pesticides (POPs residuals, in particular) included: (i) gaining the information on-site concerning the status of pollution sources, the nearest risk receptors and the potential for contamination spreading; (ii) establishing the degree of environmental pollution with POPs; (iii) integration of data gathered on-site with relevant digital map layers, information from topographical maps, aero-photo images; and (iv) calculation of "hazard indexes".

Establishing the degree of POPs contamination of sites was one of the major elements of site assessment and one of the main constituents for POPs hazard index calculation. It was implemented a "diagnostic" sampling program at all investigated sites consisting in taking one composite soil sample at every identified potentially polluted site, which allowed finding out if specific POPs were present at the site. Composite sampling consisted in mixing multiple individual samples taken from different locations on site, into a single sample[1]. Samples were transported to the laboratory where they were stored, dried up, homogenized, combined in one single sample per site and preserved for further analysis under controlled conditions according to the standard laboratory requirements.

Besides composite soil samples (as defined above), waste samples were taken from chemical piles/remains found at some old storage facilities. Those usually represented a mixture of obsolete chemicals with construction materials and soil. At several locations, water samples were taken in specific situations (e.g. wells/springs in the immediate vicinity of sites or groundwater seepage on-site). The information about the POPs level and spectrum in those matrices was used for the evaluation of additional risks for the environmental and public health.

The laboratory analysis of samples was conducted by gas chromatography in the certified laboratory of the Institute of Geology and Seismology (GEOLAB) of Moldovan Academy of Sciences. All analytical works were made in accordance with the Quality Management procedure (ISO 17025).

Finally, the POPs sites assessment culminated in calculation of a site hazard index, which integrated different elements of information, collected during site investigation namely the status of pollution sources, data on the degree of soil pollution on site, the potential for dispersion of the contamination spot, and the nearest risk receptors.

POPs environmental pollution database

A POPs environmental pollution database has been developed in order to ensure a structured management of POPs information to support effective decision making process at the Ministry of Environment.

The proposed integrated GIS system for POPs data mapping and analysis (Fig.1) allows effectively storing, managing and presenting POPs information such as geographic locations of the POPs sites, concentrations and other related parameters as well as distribution of health and environmental hazards. The system has client/server configuration with the following components:

- Integrated spatial (GIS) POPs Database based on SQL Server Express platform that supply data to below components;

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[1] Preparation of Soil Sampling Protocols: Sampling Techniques and Strategies. EPA/600/R-92/128 July 1992

- Desktop GIS toolset using ArcGIS platform, that delivers effective automation, management, editing and analytical functionality to the POPs data acquired in the field;
- POPs Web Mapping Application developed on ArcGIS Server, NET and FLEX platforms.

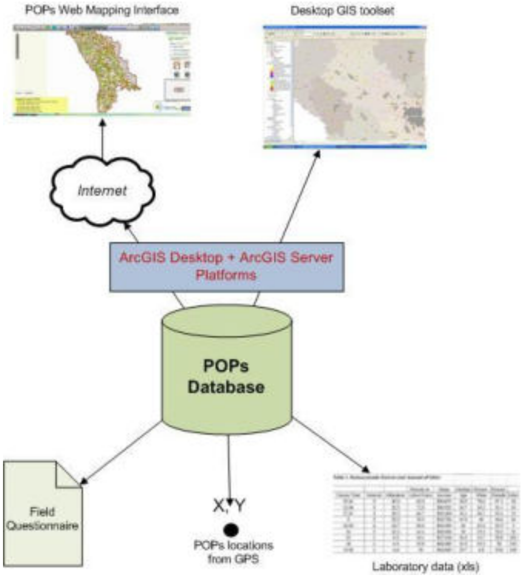

Fig. 1. Scheme of the integrated GIS system for POPs data mapping and analysis

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. For example, the database administrator would have the ability to add new spatial and non-spatial tables, add and change fields and their basic characteristics, change values for the records in the database. 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. Data incorporated in the database were fully based on the Reporting Format requirements (the field questionnaire completed by the operators on-site). In the same time, the data on POPs sites included in the database are linked with other types of information obtained in the field, including:

- Electronic form of questionnaire, ensuring the access to the original information obtained during the field investigations;
- Electronic form of sites general layout drawn by the field operators on-site;
- Photo-gallery providing a visual of the status of major infrastructure on POPs sites and surrounding neighborhood areas;
- Data on soil contamination on POPs sites provided by GEOLAB and presented under the Reporting Format requirements.

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.

The Reporting Format is based on the field questionnaire. In order to ensure that the questionnaires are filled with enough accuracy and under standardized procedures technical instructions for field operators were developed, treating the whole range of issues of concern during the field investigations, e.g. identification of main risk receptors, photo-reporting, sampling, etc.

The Reporting Format also simplify the procedures for data checking before putting into the database and help to ease new data incorporation. As a part of the Reporting Formats developing activity a special database module was developed for standardized presentation of laboratory results. The Reporting Format regarding sampling and analytical data was developed in a manner to have potential for including different environmental matrices (soil, water, air, biological samples) and for fitting various monitoring schemes, e.g. identification of POPs sites hazards or contamination dispersion.

The GIS system both desktop and web is to be integrated into daily practices of the Ministry of Environment specialists helping the authorities to define the action needed against their possible plans for the POPs sites land use and necessity for clean-up actions.

A manual for system end-users was issued in two languages (English and Romanian). The manual covers the methodology on how to execute thematic mapping in the system, how to add more sites with relevant information and publish new projects on the web.

2. 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 territorial distribution of POPs sites averaged by districts is presented in Fig. 2. The national average figure is 0.05 sites/km^2 or one site per 20 square kilometers.

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.

Throughout the country, the main type of pesticide infrastructure was represented by storage facilities (45% of the total number of installations), followed by blending stations (34%), evaporation reservoirs (13%), helicopter platforms (5%), and illegal pesticide dumps (3%).

Despite the fact that the pesticide dumps formed the lowest category of sites by number there were found not less than 73 such sites, which is quite an important figure given the illegal character of these practices.

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 (i.e., pesticide storage facilities, blending stations, helicopter platforms and evaporation reservoirs, without considering the illegal pesticide dumps), less than 9% from the total number of constructions (200 objects) were found undamaged and those were only storehouses. Among other types of infrastructure not a single one shown lack of damages.

Twenty four percent of the installations were evaluated as slightly damaged while 31% were found destroyed. In about 25% of cases only the basements of installations were discovered while for the rest of 11% of cases just the places where pesticides have been handled in the past were established.

Among destroyed installations, the share of storehouses was 22% (156 installations), blending stations – 47% (332 installations), helicopter platforms – 6% (41 installations), and evaporation reservoirs – 25% (174 installations). Among those installations for which only basements were found, the share of storehouses was 65% (362 installations); the share of blending stations – 30% (167 installations), and the rest were helicopter platforms. Among the sites where previously pesticide infrastructure was present (now completely wiped out), 63% (155 installations) were former storehouses, 32% (78 installations) were blending stations and the rest were former helicopter platforms.

Among identified illegal pesticide dumps, two thirds or 49 dumping places were covered by earth while 24 places were found uncovered.

3. 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 ∑ DDT, ∑ 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).

The pollution of POPs sites with DDT and – to lesser extent – with HCH can be defined as widespread. The share of sites contaminated with chlordane (31%) and heptachlor (22%) is also significant. Less number of 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 of soil contamination with POPs pesticides at some investigated sites, in the order of hundreds and even thousands of mg/kg. The concentrations of the five mentioned POPs pesticides varied in the interval from detection limit to 616 mg/kg for chlordane, 4838 mg/kg for toxaphene, 505 mg/kg for heptachlor, 3148 mg/kg for sum of DDT metabolites, and 4216 mg/kg for sum of HCH isomers.

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 were studied separately from soil samples on 42 sites. The waste samples 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 Fig. 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, measures preventing the access of and contact with the population as well as remediation measures to minimize pollution spreading are to be envisaged.

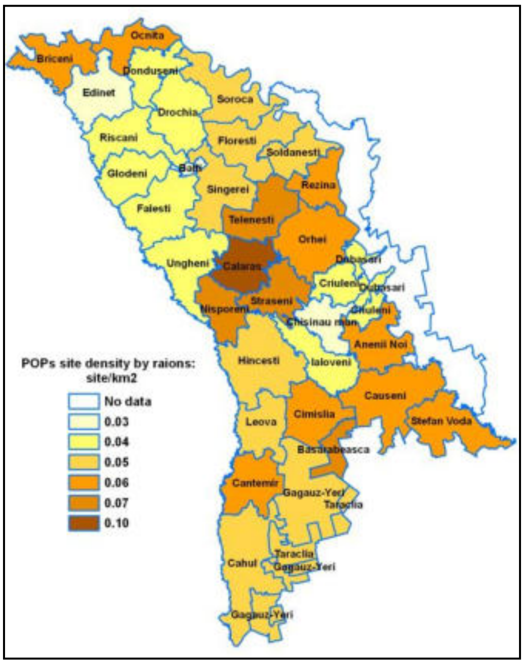

Fig. 2. Territorial distribution of POPs sites by districts

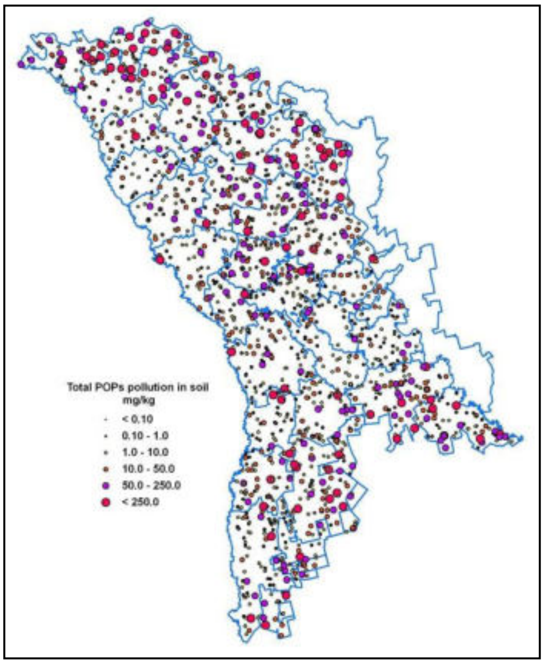

Fig. 3. Spatial distribution of contaminated sites

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.

4. PRIORITIZING OF POPs CONTAMINATED SITES

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

The POPs sites hazard assessment

Besides 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 the 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 didn't 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.

The proposed site hazard assessment is based on three pillars, similar to the classical risk assessment elements:

- Level of Contamination,
- Risk Receptors, and
- Pollutants Distribution Potential.

The integration of these three conceptual elements into the total site score system is providing an integral approach for site classification, which is a well-approved international practice. Nevertheless, the major focus of the site hazard assessment tool formulated under the current assignment was to adapt the methodology to the local conditions and to the existing in-country capacity, thus allowing the district ecological inspectors and the database administrator at the Ministry of Environment to implement the assessment after project termination.

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 follow:

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 %

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 only one – probably the 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 from the way 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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[2] A Federal Approach to the Contaminated Sites / Dillon Consulting Limited, Ottawa, Ontario, November 1999.

ALTERNATIVE APPROACHES IN BIOREMEDIATION ENGINEERING

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KEYWORDS
Biodegradation, bioremediation, supporting processes, biofilms, syntrophy, microbial consortium, autochthonous microorganisms

ABSTRACT

There are stereotypes that bioremediation is biodegradation. In fact, biological conversion of contaminants into less harmful or nontoxic compounds really holds the majority in the bioremediation. On the other hand, it is very necessary to understand the processes based on non-biodegradation nature, which can play a crucial role in the functioning of the entire bioremediation system. In the first part of the paper, the attention turns to the positions of anthropogenic contaminants in microbial metabolism. The contribution is about significant functional diversity, whether it is more frequent the position of carbon source, or it is position of reducing equivalent source. Why do some ambiguities exist in alternation of terminal electron acceptors? On this occasion, it will be introduced a short view (as a special supplement) on the infrastructure and potentials of anaerobic microbiology laboratories in clean-up technologies. The second part of the paper develops the issue of supporting processes of bioremediation technologies (syntrophic interactions, new trends and knowledge associated with biofilms in contaminated systems, etc.) and it will focus primarily on the performance summary and indirect interactions between microorganisms and their products with contaminants. Bioremediation can benefit from their conversion to technological tools. Both parts offer a clear theoretical framework and then build on it a selection of some practical applications, experiments and tests. The purpose of the paper would be to change stereotypes and give perspective in the bioremediation as extremely dynamic, flexible and responsive field

Fig. 1. The key device in environmental microbiology – glovebox for anaerobic manipulaton with microorganisms (laboratory of EPS in Kunovice)

Bioremediation is an integral part of biotechnology as the use of biological agents in applications to remedy environmental damage and for environmental friendly waste treatment. It was founded in the 60th years of the last century and helped to develop it natural processes in the soil that has been contaminated by petroleum products. George Robinson, founder of the first remediation company in the world (U.S. Microbics, Carlsbad, California), he noticed a decline in crude oil in the soil. Series of experiments discovered the role of bacteria in the break-down process. Further research and development built the foundation for bioremediation engineering, as is now well known and used. Natural attenuation is a natural reaction to the presence of undesirable environmental substances. 95% of biodegradation processes through adapted populations sophisticated interplay of abiotic processes (sorption, convection, diffusion, etc.) characterizing these natural processes (Mikes et al., 2010).. An important factor is the amount of contaminant; biological processes are suitable to be applied in systems that need downstream clean-up processing leading to the desirable environmental standards.

Bioremediation is based on two concepts - bioaugmentation and biostimulation. Bioaugmentation is based on a targeted introduction of suspensions of suitable microorganisms into contaminated system. This must be preceded by isolation and characterization of culturable microorganism. Then, the procedure should be developed on large scale cultivation, during which a care must be taken to preserve abilities and characteristics of particular microorganism. Subsequently, in a suitable growing season bioaugmenation agent (microbial suspension) is applied to the contaminated system. Due to the fact that many of biodegradation processes are determined by the plasmids, there is a real risk of loss of skills due to the microbial strain was chosen as the the fundamental part of bioaugmentation agent. Large reserves exist in conservation of suitable biodegradable microbial strains in the collections of microorganisms. At present, the best solution shows lyophilization (gentle drying using cryoprotectants at low temperatures based on sublimation). Not every laboratory of a clean-up company has this equipment. Even greater risk may result from an adaptation of the organism on artificial and stable conditions, which ultimately causes the loss of the ability to adapt quickly to a much harsher and volatile profiles of real conditions. The worst finding (using modern molecular-biological methods) is the observation that in the frame of in situ applications, the chances of survival brought by microorganisms (and the creation of a stable population in the contaminated site) is practically zero. For these reasons, bioaugmentation seems to be objectively a way for on site applications, and some ex-situ solutions, which are more likely to maintain stable conditions in the contaminated system.

Biostimulation is based on the adapted population occurring on contaminated site. They are able to survive and find the competitive advantage. The principle of biostimulation is nothing more than a thorough knowledge of the situation at the contaminated site from the perspective of microorganisms. Based on its interpretation then weaknesses have to be revealed and appropriate treatment to improve biodegradation performance has to be found. Most often it deals with a supply of the source of some of metabolically significant substances. There are three areas that can be affected. Usually better carbon source (either as a supplement to the primary metabolism or bet kometabolismus) is sought, further reducing power equivalent (electron source for chemotrophic population) may be supported - if not the same as the carbon source (lithotrophy versus organotrophy) or better terminal electron acceptor (either a supply of air for aerobic processes or stimulation of anaerobic respiration). Artificially supplied support resources are often surfactants or substances releasing oxygen. Biostimulation is closely related with combined remediation technology. Abiotic process (eg, pump and treat, dredging, clean-up washing) or the parallel solution (venting, air sparging) often play a role of the stimulating agent for the most effective solution. For these reasons, a combination of remediation technologies (treatment train approach) speaks in the present as the most progressive concept of remediation. The reason is not only a good chance to achieve environmental standards, but also the credibility of the work (if reasonably designed the system of control and monitoring), but also a solution that is clearly low-cost strategy.

Contaminants in microbial metabolism can serve as a carbon source (such as phenol or crude oil hydrocarbons). Mostly the same compound is also a source of reducing equivalents (organotrophy, the source is an organic compound). In this case, however, it may be substituted by an inorganic substance, if the nature of the metabolism has a lithotrophic character (sulfides, iron, ammonium, etc.). Lithotrophic bioremediation is a major challenge for better application in practice, not only in the biodegradation, but especially in the processes of toxic elements stabilization. This stabilization is an example of indirect positions of the contaminant in microbial metabolism, the hydrogen sulfide as a product of sulfate reducing bacteria acts as a precipitating agent producing very little soluble sulfides of toxic elements. Limiting of the mobility in these substances reduces environmental risks. The position of contaminants on the place of the source of energy is very often. Alternation of energy sources (represented by the covalent bond) by the fixation of light energy takes place in natural processes, but the specific engineering applications in bioremediation is rather academic research (phototrophic bacteria, cyanobacteria). On the contrary, the situation is much better if the contaminant acts as a terminal electron acceptor (such as sulfates, nitrates, As (V), Cr (VI), the PCE and TCE, etc.). The remarkable position of the contaminant is its role in cometabolism. Microorganism has met all needs and produces in excess of a few specific enzymes that simultaneously transform the contaminants into non-toxic form, without energy profit for the microbial cell. Aerobic cometabolism of chlorinated ethylenes using methanotrophic bacteria is known, but there is also anaerobic cometabolism, such as elimination reactions of vicinal hydrogen and chlorine atoms in chlorinated hydrocarbons in the absence of oxygen (Häggblom, 2003)..

Tab. 1. General comparison of clean-up methods

District	**bioaugmentation**	**biostimulation**	**natural attenuation**	**abiotic approaches**	**treatment train technologies**
in situ	weak	high impact in treatment train	high	in cases of strong contamination	the best strategy in Europe
ex situ	strong position	alternation	weak	strong solution	future trends
on site	in bioreactors	alternation	weak	clever solution	integral part
costs	low	middle	low	very expensive	promising CBA
effectivity	low	in some cases	in USA	arguable	arguable
knowledge	disputable	satisfactory	many questions	well known	many questions
future challenge	HGT	big	on large sites	as a complement	the biggest
sustainability	today very weak	satisfactory	enormous	weak and expensive	middle course

Reductive dehalogenation, SRB, anaerobic cometabolism, many forms of lithotrophic metabolism is just a selection of processes that must be studied, analyzed and tested under anaerobic conditions (Schink, 1997). This work is not enough in the usually equipped laboratory. It must be equipped with a glovebox and an anaerobic cultivator, which serve for simulating of anaerobic conditions. EPS has this infrastructure and is actively devoted to anaerobic bioremediation potential usage in practice. Specifically, the taxa of the genus *Thiobacillus*, further SRB and denitrifying biodegradation or break-down process in crude oil biodegradation based on the amendment of some simple dicarboxylic acids. When a laboratory is declaring the analysis of anaerobic microorganisms in environmental samples and does not have the above-mentioned equipment, then it is a deception in the case of commercial relationships. Although otherwise, in such way specified microorganisms are, at best, only facultative anaerobes.

Recent metagenomic studies lead to the conclusion that successful bioremediation is based on several key factors. First, it applies the potential of unculturable microorganisms (some studies claim that this is a 99.9% of all microbial taxa on Earth). In close connection, the system of syntrophy must be fully functional. A particular example is the application of lactate in sites contaminated with chlorinated ethylenes. Lactate is utilized by microorganisms that fail in transformation of chlorinated ethylenes. However, its activities lead to the production of gaseous hydrogen, carbon dioxide and acetate, reducing the redox potential of the system and create the suitable conditions for the bacteria, which are responsible for microbial dehalogenation processes (respiration chlorinated ethylenes or its direct metabolic transformation). Another example may be the subsurface contaminated by petroleum products. The key skill in bioremediation for petroleum hydrocarbons is the production of microbial surfactant. These compounds inetrrupt the phase interface (between aqueous and non-polar fractions (petroleum hydrocarbons)). There are also strains that are hyperproducers of biosurfactants, including yeast. Thanks to this interplay of described groups, bioremediation performance reaches its excellence (Holliger, 1996).

A big disappointment is coupled with genetically modified microorganisms for bioremediation applications. Not only because of legislative restrictions. Mainly enormous vulnerability and inability to create a viable population in the real environment led to the practical end of this strategy. The phenomenon of microbial biofilms is still promising for bioremediation practice. These *cities of microbes* are a perfect projection of all (above mentioned) factors (syntrophy, colonization of surface, stability of the consortium). The power of biofilm is hidden in the stable adaptation without major fluctuations. This is the preferred strategy for survival in the real world. Unfortunately, there is a lack of answers that would make the concept of stronger biofilm more usable in bioremediation applications, especially in the in situ applications. Biofilm is the perfect interplay of particular microbial groups. It is a stable metabolic performance, protecting cells comprising it, and it is the base camp for further colonization environment. Bioaugmentation fails obviously from the crucial step: Implementation of bioaugmentation agents into the biofilm of adapted indigenous strains in the contaminated area is not successful.

Bioaugmentation do not need to end up as a strategy, which has not worked. Flexibility and adaptation of microorganisms to real conditions is given by the so-called horizontal gene transfer. Besides the vertical transmission of genetic information from mother to daughter cell or direct cell division, there is a possibility to pass the plasmids among bacteria without the taxonomic affiliation. A number of genes for specific bioremediation process or for the resistance are encoded on plasmids. Using the transformation (plasmid adoption of dead biomass), the conjugation (formation of conjugation channel between two cells) or the transduction (bacteriophage is a vector of the plasmid) incredibly improves the metabolic memory of natural consortia. This way has enormous potential for engineering and its use is very similar to the bioaugmentation.

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THE FAO ENVIRONMENTAL MANAGEMENT TOOL KIT VOLUME 5; A SYSTEMATIC AND PRAGMATIC FRAMEWORK FOR DEALING WITH PESTICIDE CONTAMINATED LAND PROBLEMS FOR USE IN LOW TO MIDDLE INCOME COUNTRIES

Russell Cobban – Richard Thompson – Kevin Helps

KEY WORDS
Risk assessment, contaminated land, POPs, pesticides, FAO EMTK, FAO Rapid Environmental Assessment (REA)

ABSTRACT

The United Nations Food and Agriculture Organization (FAO) has for many years been involved with the safeguarding of obsolete pesticides, including persistent organic pollutants (POPS), in projects worldwide. In many cases the poor management of stocks above ground has led to a legacy of below ground contamination which has historically been dealt in an on an ad hoc manner. In dealing with above ground stock FAO has developed a series of tool kits, the Environmental Management Tool Kits (EMTK) numbers 1 -4, in order to structure the safeguarding process and minimise risk to human health and the environment. FAO is now intending to develop a 5th tool kit; EMTK 5 that will bring a similar systematic and pragmatic approach to sites contaminated with pesticides for countries participating in FAO related programs. The EMTK 5 will condense and clarify much of the guidance available internationally for use in lower and middle income countries where the capability to implement projects is more limited in terms of resources and technical understanding. This paper presents a structure for the EMTK5 and investigates methods that FAO can use to improve contaminated land assessment and risk management practises in countries that are appropriate to the budgets available and the often difficult and remote locations in which projects are implemented.

BACKGROUND AND INTRODUCTION

Within the United Nations Food and Agriculture Organization's (FAO) remit of reducing world hunger it has been extensively involved with pests and pesticides management. For some decades FAO has also been committed to the prevention of accumulation and the safe disposal of obsolete pesticides of which there is in the order of [1]half a million tonnes worldwide. The Pesticide Management Group of the Plant Production and Protection Group (AGPM) of FAO has been involved in the safeguarding and disposal of pesticides in over 40 countries globally since 1992. Based on the experience gained over the past 20 years FAO has looked to develop tools which allow a risk based prioritisation of pesticide storage locations taking into account potential impact on both public health and the wider environment. This has lead to the development and publication of a series of technical guidelines, the Environmental Management Tool Kit Series (EMTK 1 - 4). The methodologies presented in the tools have been developed to provide a sound technical baseline for implementation of pesticide inventory and safeguarding projects in developing and developed countries in a number of regions across the globe. They have a solid foundation in international regulations from the US and Europe and so can be considered as complying with international best practice for worker and environmental safety. The tool kits were developed with financial assistance from the EC, GEF and Government of the Netherlands.

The tool kits aim to meet the needs of countries setting out on the long and complex process of managing their obsolete pesticide stocks effectively. Coupled with technical guidance on pesticide inventory and access the FAO Database "Pesticide Stock Management System " (PSMS) they provides country teams with simple guidance on how to gather and interpret information on obsolete stocks, and use it to develop a coherent, risk-based strategy for the environmentally sound management of those obsolete pesticides. Through consultation with experts and country teams from developing countries, the series of methodologies developed is based on practical experience of project implementation. The tool kits seek to avoid very theoretical and impractical methods that rely on high levels of national capacity in such areas as EIA. Although experience in environmental issues, chemical management and such concepts as hazard and risk are an advantage, the accompanying training courses provides the necessary skills to finalize a meaningful set of outputs. Adoption of the tool kit methodologies makes it possible to manage obsolete pesticides in ways that are safe and

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1 (UN FAO, n.d.)

environmentally sound. The kits are supported by a series of training modules which have been consolidated into a Module of the Pesticide Risk Management Postgraduate Diploma course which is currently offered to students through the University of Cape Town and which is planned to be adapted for use in the former Soviet Union countries under support from the European Commission.

Despite the removal of the above ground stocks from sites where pesticides have been previously stored pesticide legacy problems have developed that affect the ground beneath the sites and the groundwater passing through. These sites present an on-going risk to human health and the wider environment and in many cases pose a greater risk to both than the pesticide stockpiles which are often sent for environmentally sound disposal. In response to this need and in recognition of the risks posed by uncontrolled releases of POPs and pesticide FAO has taken the initiative to develop a fifth tool in the EMTK series, EMTK 5 ,through the support of the EC as part of a larger pesticide management initiative in the former Soviet Union. The guidance will also be transformed into a new Module in the Post Graduate course on Pesticide Risk Reduction. The former Soviet Union region is particularly affected by the impacts of pesticides which have been sent for long term storage in burial locations. The quality of the storage sites varies greatly with no standardisation of construction of siting of the facility in terms of risk planning. Many burial locations therefore lack any form of barriers to prevent dispersion of the waste into the wider environment and the risks to public health and environment are considered as significant. The provisions of the Basel and Stockholm Conventions prohibit the disposal of POPs pesticide waste at a concentration of greater than 50 parts per million. Signatories of the Conventions are therefore obliged to develop an action plan detailing how the risks from any sites where POPs pesticides are buried will be addressed (NIP Guidance ref). The sheer number of such storage locations and wide geographical spread of the burial sites makes assessment and risk-based prioritization key to formulation of any longer term programme on risk reduction. The approach will seek to address the problems posed by land contaminated by pesticides in a pragmatic manner similar to the other tools in the series.

EXISTING APPROACHES TO CONTAMINATED LAND RISK ASSESSMENT AND RISK MANAGEMENT

In the context of contaminated land, risk assessment and risk management have been applied for the longest period and most directly in the USA. The investigation of superfund sites is a formalised process used to determine the potential for human impacts and to evaluate risk management strategies. [2]The US experience, however has shown that over a 28 year period and the expenditure of almost 30 billions of dollars to remediate 1141 sites, at an average of 26 million dollars per site, that the risk assessments conducted are often overly conservative and the risk management systems very capital intensive.

Many other countries and international agencies across the world have issued guidance directing assessment and risk management towards contaminated land problems in general; much of this guidance is very comprehensive and extensive. The information available is related towards a particular population, location and legislative system. Each country has its own objectives for contaminated land guidelines that may not be relevant or transferable to a frame work that is intended for use in low and middle income countries.

The development of guideline values or screening levels against which the contaminant levels are measured to gauge the level of risk is a good example. The benefit of using screening levels is clear and is relevant to working in the developing world environment. Screening levels permit non-specialists and other stakeholders a clear and simple method of classifying the risk presented by a site. Guideline values focus further investigation and detailed quantitative risk assessments (DQRA) to the sites where quantitative risk assessment is required and can considerably reduce costs as they have a more limited requirement for data and expertise. However, there are numerous guideline levels that have been published by many countries; derivation methods differ from country to country and are based on differing assumptions such that the guideline used, for example the Dutch system, may not have a basis for use in developing countries.

There are more than [3]1700 chemicals functioning as pesticides that could possibly be encountered on contaminated sites. Screening values for only [4]17 compounds have been developed by the Netherlands and this situation is similar for other countries across the rest of the world. The [5]World Health Organization has a list of 33 pesticides for which WHO Drinking Water Quality Guidelines have been developed.

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2 (US Government Accountability Office, 2008)
3 (Wood, 2013)
4 (Netherlands Ministry of Housing, Spatial Planning and the Environment, 2009)
5 (WHO, 2006)

DIFFICULTIES OF OPERATING IN LOW AND MIDDLE INCOME COUNTRIES

Operational difficulties of conducting assessments in countries where FAO routinely operate include lack of investigation equipment, lack of adequate analytical facilities, difficult communication and lack of background information. In terms of implementing risk management strategies the sites are often remotely situated where infrastructure is poor and lack basic facilities such as power and water that the more innovative risk management techniques require.

Low and middle income countries tend not to have strong institutions or legislation relating to environmental policy. Frequently the institutions lack the expertise to deal with the challenges posed. FAO member countries often rely on external assistance to address environmental problems such as the legacy of obsolete pesticides.

WORKING WITH PESTICIDE CONTAMINATED GROUND

Frequently FAO field inventories of stock held, indicative of what lies beneath the ground, show that the obsolete pesticides involved are persistent and toxic to both man and the environment. The POP pesticides DDT, Lindane (gamma HCH), HCH (including alpha and beta isomers) and Endosulfan occur in the ranked top 15 of pesticide quantities that occur in the obsolete stock of FAO surveyed sites across the world.

Tab. 1. [6]Top 15 Obsolete Pesticides occurring by mass in FAO surveyed stores across the globe

Rank	Pesticide	Quantity (kg)
1	sulphur	518,203
2	DDT	467,032
3	endosulfan	406,329
4	malathion	388,605
5	HCH	316,645
6	deltamethrin	275,832
7	parathion	239,970
8	carbaryl	178,953
9	pirimiphos-methyl	149,217
10	2,4-D	148,129
11	cypermethrin	138,070
12	glyphosate	105,273
13	fenitrothion	103,439
14	lindane	93,827
15	hexazinone	77,332

Note: there are many unknown materials not included in the table, the identity and hazard of which is difficult to determine without further assessment

Risk management of ground contaminated with pesticides often requires techniques that are energy intensive, non-sustainable and very expensive. Furthermore, more recently developed and more innovative engineering techniques coming on line in western countries are difficult to implement and expensive to operate in the challenging field conditions encountered low to middle income countries. The very nature of POP pesticides means that bioremediation techniques are very often ineffective or take a long time to have an effective.

Funding for contaminated land clean-up in low and middle income countries

An underlying tenet of contaminated land risk assessment and risk management is the ‘polluter pays’ principle whereby the party responsible for producing pollution is made responsible for paying for the damage done to the natural environment; this approach is advocated across Europe, North America, New Zealand and Australia. In low and middle income countries many of the legacy problems of pesticide contaminated land originate from pesticide stock mismanagement and frequently cannot be attributed to any one individual or organization. In these countries contaminated land is low on a long list of the states’ priorities, it is for these reasons that clean-up of pesticide contaminated land currently relies on donor assisted projects. Unfortunately this is not sustainable; in the long term donors cannot be relied upon and increasingly funding for this type of work is becoming ever more constrained. There is therefore the imperative to develop sustainable pesticide management

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6(UN FAO, 2013)

practises such as Integrated Pest Management (IPM), and to reduce the toxicity and quantity of pesticides used. Another imperative is to develop lower cost solutions for the risk management of pesticide contaminated land. In the future it is hoped that as countries become wealthier that the 'polluter pays' principle will become more relevant outside OECD countries.

The challenge for FAO

The challenge for FAO is to develop a contaminated land assessment and risk management framework that is:

- flexible for use in FAO member countries worldwide;
- based on sound scientific principles;
- transparent;
- relatively easy to use and implement; and is
- cost effective.

The challenge for EMTK5 is not to reinvent procedures and processes that are already in existence but to collate and adapt relevant information that is available and focus it for use on pesticide contaminated sites in a clear and pragmatic fashion.

Risk Based Assessment

The premise of the FAO contaminated land framework is that it will be risk based and directly related to the concept of the 'source –pathway – receptor' principle. Interventions will only occur on sites where it is established that all three entities are present in relation to a site. Effort will be made to ensure that this is established as early as possible during risk assessment, using tools such as the FAO Rapid Environmental Assessment, so that resources are not spent unnecessarily later on.

Tiered Risk Assessment

In general terms risk assessment of contaminated sites is a tiered process; each tier requires an increasing level of data and corresponding increase in external assistance (with respect to developing countries) and also increasing cost. There is a balance to be struck between of the level of confidence of an investigation and the cost required, the funds for which, as has already been stated, are usually minimal. It is intended that bulk of FAO investigations will be restricted to Tier II investigations whereby the use of guideline levels will be used for risk assessment. For grossly contaminated sites Tier III investigations may occasionally be necessary that comprise site specific modelling in order to more fully understand the site conditions for the purposes of risk management.

Proposed EMTK5 Framework

The chart in Figure 1 below presents the basic steps required for the proposed framework.

Step 1: Pesticide Contaminated Site Identification

Member countries will identify and select sites potentially contaminated with pesticides. Those countries that have been participating in the survey of pesticide storage locations using the PSMS will also have a record of contaminated sites that will be considered for further intervention following the next step of prioritization.

Step 2: Site Prioritisation using the FAO Rapid Environmental Assessment

The limited resources available for most projects require that funding is direct towards sites that are in most need of intervention. FAO have been developing a tool, the FAO REA, that will be used to prioritize sites for further investigation and, if necessary risk, management. The methodology developed for the REA is composed of two distinct stages. The first (Desk Screen) is a method for prioritizing sites from the existing national database for preliminary site visits. The second stage consists of the preliminary site visit during which a questionnaire is completed and a limited number of samples are taken. The Desk Screen relies on GIS information (soil type, slope, proximity of water) and chemical specific information (quantity, half-life), and provides an output (low, medium, or high priority) to determine which sites should be prioritized for the second stage. It is important to recognise

Step 3: Preliminary Desk Study of top sites prioritised, formulation of preliminary conceptual model and the sampling and analytical strategies

Those sites that have been prioritised as being in need of further investigation and risk management will then be subjected to a preliminary desk study. The data collected during the prioritisation stage will form the basis for the development of a preliminary conceptual site model. The FAO CSM tool will allow users to visualise the fundamental issues affecting a particular site in order to plan and develop the following stages of risk assessment. Guidance will be given as what other information is required to complete the preliminary desk study.

This stage will also comprise a tool that will help users to select and design sampling strategies required for the detailed investigation. Recommendations will be made for the levels of confidence at which investigations should operate and the minimum number and type of samples for a given situation. Levels of funding available mean that this it is not always possible to manage investigations at a particular level of confidence; guidance will be given on the use of basic statistical techniques to ensure that the level of confidence to which an investigation is being conducted is, as a minimum, understood.

Further guidance will be given on quality control and quality assurance of investigations so that the confidence in the results of an investigation can be maximised.

Step 4: Detailed Investigation

Prior to the implementation of risk management this phase is likely to be the most capital intensive for projects and most difficult to organise. Guidance will be given on cost effective types of investigation equipment available and those types of investigation techniques that are more likely to be successful in the field.

For investigations overseas robust project management is essential. In a similar vein to EMTK4 guidance will be given as to how investigations can be conducted safely and as accurately as possible. It is intended that Standard Operating Procedures (SOPs) for basic investigative techniques be provided to give a minimum standard for assessors to operate to and also allow countries or organizations with more limited experience to be able to carry out investigations without intervention.

Step 5: Detailed Quantitative Risk Assessment

The underlying principle of the FAO risk assessment will be comparison of measured levels of contamination against risk based screening levels. Guidance will be given as to the correct use of available screening levels and under what circumstances they are appropriate for use. Additional information will be available to assessors so that they are able to understand analytical results received from laboratories and how and in what form they may be compared to screening levels.

Step 6: Site Specific Risk Management Plan

A site specific risk management strategy will be developed for each site that is based on mitigating the pollutant linkages identified by the risk assessment. This will comprise of the selection of appropriate techniques via matrix analysis and SWOT techniques to ensure that the strategy is both effective and complies with best practise, local legislation and international conventions such as the Stockholm Convention. Each element of the risk management strategy will undergo further analysis to produce an Environmental Monitoring Plan. This will be similar to the analysis of safeguarding strategies in FAO EMTK3 whereby mitigation measures for the risks identified to the project are specified together with the institutional responsibility for carrying out each. An important part of this will be to develop a budget for the Environmental Monitoring Plan.

Step 7: Countrywide Environmental Management Plan

The countrywide contaminated land environmental management plan will be a component of the output from EMTK3 and will be presented together with the safeguarding and disposal strategies. A summary of contaminated sites, pollutant linkages, and quantity of contaminated soils, risk management strategies and techniques will be presented. This will allow a rationalization of strategies at a countrywide level that will take advantage of, for example, economies of scale and waste management infrastructure postulated by the safeguarding and disposal strategies for each country.

CONCLUSION

It is planned that Volume 5 of the FAO Environmental Management Tool Kit will fit into the mould of the existing documents in the series. It is hoped that EMTK 5 will aid low to middle income countries in tackling pesticide contaminated land problems using a clear and pragmatic framework for risk assessment and risk management. EMTK 5 will help project teams to complete projects under difficult operating conditions with often restricted budgets and where conventional risk management techniques may not be possible.

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RAPID ASSESSMENT OF POPS PESTICIDE CONTAMINATION SITES – – A SIMPLIFIED METHOD AND INNOVATIVE DATA MANAGEMENT SYSTEM DEVELOPED FOR VIETNAM

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KEYWORDS

Pesticides, persistent organic pollutants (POPS), site contamination, rapid environmental assessment (REA), sampling, geographic information systems (GIS), risk assessment.

ABSTRACT

Sites contaminated with persistent organic pollutant (POPs) pesticides are a common issue in low and medium income countries. The reasons for the contamination are general linked to a failure in the life-cycle management of pesticides as presented in the Code of Conduct on Pesticide Management (FAO/WHO 2012). Much work has been done previously on developing risk based criteria for the prioritization of sites where pesticide stockpiles are present (FAO EMTK volume 1 and PSMS system). Similarly there are a variety of systems available for the investigation and risk assessment for sites contaminated with POPs and other hazardous materials. Most of the assessment tools involve extensive sampling to characterize the risks which is often prohibitively expensive and impractical given the local capacity for analysis. Clearly, to reduce impacts on public health and environment there is also a need to assess and prioritize sites to allow for greatest risk reduction during any planned clean up action. However, many countries have limited funds and expertise to conduct such assessments.

This paper presents a newly developed rapid assessment system to facilitate preliminary assessment of POPs contamination sites by persons with limited expertise and at little cost. The system was developed for the Vietnam Environment Administration by Blacksmith Institute (New York, USA) under a contract with the Food and Agriculture Organization of the United Nations (FAO) using resources from the Global Environment Facility (GEF). It includes innovative methods to integrate existing knowledge about sites with Geographic Information Systems (GIS) data through a Microsoft Excel based template. The two-step method involves 1) a preliminary site identification and prioritization based on limited historical site information, followed by 2) on-site visits to locations defined as priority sites during step 1. During site visits, investigators determine field conditions, collect basic demographic, geographic and geologic data, and conduct limited but targeted environmental sampling. Protocols developed by international assessment specialists guide the site visit process. The results of field visits, combined with the GIS data and a further developed prioritization algorithms, allow rapid and cost effective initial prioritization of sites for further assessment and action.

INTRODUCTION

Pesticides have been used extensively in agriculture since the middle of the 20th century. Several important studies in the United States, starting with the publication of Rachel Carson’s “Silent Spring”, and elsewhere on the potential environmental and human health impacts of pesticides led to their stricter regulation in the 1970s. As a result of national and international efforts to address health and environmental concerns about persistent organic pollutants (POPs) pesticides, the use and application of POPs pesticides has been substantially reduced since the 1970s and emissions have steadily declined (Morner 2002, Lohmann 2007). Despite decreasing use, Pesticide POPs will continue to be a challenge for decades to come, as there are large amounts of legacy POPs stores and POPs wastes in landfills or other locations. For example, an initial estimation assesses 2-5 million metric tonnes of wastes from lindane production (Vijgen 2006) making Lindane the most important pesticide POP. Also, some pesticide POPs use continues to be allowed, such as DDT use for controlling malaria (WHO, 2006).

The rapid decline of POP pesticide usage since the 1970s has not been uniform among nations. High-income countries, mostly in Europe and North America, ceased production and application of most POPs pesticides in the 1970s, followed by low- and middle-income countries and the Soviet Union. By the mid-1980s, there was significant action to reduce or control POPs releases in much of the world. However, as late as 1996, most countries had not banned POPs completely and active use continued in many lower and middle income countries

(Roberts 1998). Continuing global concern about POPs led to the negotiation of the Stockholm Convention on Persistent Organic Pollutants (POPs), which entered into force in May 2004 (Gopalan 2003, Lallas 2001). The Convention, among other things, requires member states to identify stockpiles of POPs, products or wastes containing or contaminated with POPs, and sites contaminated with POPs. It also requires Parties to take appropriate measures so that POPs and POPs contaminated sites are managed in an environmentally sound manner. This includes destruction of POPs stores and, preferably, remediation of contaminated sites. As of 2013, 179 countries have signed on to the Stockholm Convention, making the Convention nearly universal in scope. (Secretariat of the Stockholm Convention 2013).

Despite the global recognition that POPs present a major environmental and public health risk, action to fully implement the Stockholm convention requirements in many low and middle income countries has been mixed due in part to accessibility of funding, political responsiveness and sound disposal options. Significant quantities of POPs pesticides remain in stores without a productive end use or feasible disposal options (FAO 2002). These pesticide stores present a range of conditions. Some are well maintained with appropriate oversight and control, including inventories, labels, impermeable containers, manned security and fencing, and ongoing surveillance. However, in many cases, especially in low or middle-income countries, these locations are poorly managed and may be source of active leaking POPs into the environment. Of the latter group, an unknown number of high priority sites actively pose a risk to human populations.

A key challenge for low and middle income countries is prioritizing their limited resources so that the most dangerous POPs stores and POPs contaminated sites, notably in terms of possible and actual impact on public health and the environment, are addressed first. These countries often have hundreds or thousands of such stores and sites, but usually do not have the resources to fully evaluate each one. Moreover, these countries may have limited numbers of people who have the knowledge necessary to do a quality site evaluation and risk assessment. This challenge has been recognized by many organizations, which has led to development of various Rapid Environmental Assessment (REA) systems. Such systems ideally would allow low and middle income countries to quickly and accurately assess sites and prioritize them for further attention in an economical manner, using staff with limited background in assessment and risk evaluation, and incorporating under the surface the experience and expertise gained throughout the world. No REA will perfectly assess and prioritize site risks, rather what is desired is an optimal balance between time, expense, expertise, usability, simplicity and, critically the validity of results in terms of allowing the ranking of sites based on relative risk.

In 2012, Blacksmith Institute (BI) was contracted by the Food and Agriculture Organization of the United Nations (FAO) to develop a risk-based rapid assessment protocol for the Vietnam Environmental Administration (VEA). The new protocol was to use the existing FAO Rapid Environmental Assessment (REA) as a starting point. VEA and others had previously inventoried some 601 POPs pesticides stores in three provinces. There was a need to prioritize these sites first for assessment visits, and secondly for remediation. As in many countries the locations in Vietnam were characterized by much of the POPs and pesticide waste having leaked from the original containers with release into the wider environment. FAO has previously developed a methodology for the assessment of pesticide products at storage locations (EMTK volume 1) but the protocol developed does not provide adequate scientific basis for the stores where the pesticides have become dispersed into the environment. This paper describes the methodology that was developed by BI to meet these ends, and further suggests that it may be adapted and successfully applied elsewhere.

Enhancements to the FAO REA Protocol

To support the development of the revised methodology for assessment of pesticide contaminated sites for FAO, BI conducted a review of seven site assessment protocols in addition to the draft FAO REA methodology. The REA methodology was developed in recognition of the gaps in the EMTK pesticide risk assessment tool which was primarily designed for assessing pesticide storage locations. The seven protocols evaluated reflected a broad cross section, including those from both the public (UN) and private sectors. Importantly, each methodology was intended to be utilized by inexpert assessors with limited experience. The following protocols were reviewed: Blacksmith ISS; FAO Environmental Management Toolkit (EMTK); Hatfield Consultants' POPs Toolkit; Industrial Development Organization (UNIDO) POPs site assessment protocol; The supplier review protocol from a major multinational pharmaceutical company, which is not targeted towards contaminated sites but evaluates a number or relevant subject areas such as container and storage risks, and management systems; FAO REA; and, the New Zealand Government developed Rapid Site Survey (RSS).

As a result of the review of existing protocols, three key revisions were identified for inclusion into the draft FAO REA methodology. The first such area was a revised sampling protocol. Several of the methodologies reviewed included a sampling regimen. In general, some sampling is seen as essential by the experts consulted by BI in order to establish or at least confirm the presence of contamination and to gain some understanding of the level of contamination to which receptors are exposed. Reliance only on historical data or visual observation is not considered to be a sound basis for understanding site risks in most cases. Various sampling regimens were evaluated with particular concern for the level of expertise required to implement the sampling, time and affordability of collection, and the usefulness of the data collected for estimating the overall site risk, among other criteria. The Blacksmith Initial Site Screening (ISS) sampling methodology scored favorably for several key reasons. Among them, the ISS has a strong emphasis on rapid and affordable implementation. The protocol includes a minimum of five and a maximum of ten soil samples for each evaluated site. Clear instructions with visual aids are provided to help assure quality sample collection. In addition the sampling component of the ISS considers multiple pathways and receptors. Populations are disaggregated by their primary route of exposure, allowing for more accurate characterization of health risks.

The ISS sampling methodology is conducive to consistent data collection. The methodology has been carried out by BI and partners in 1800 risk screenings in 47 low and middle income countries. These screenings were implemented by investigators with varying technical backgrounds and area of expertise and presented results that allowed for quick comparison and prioritization (see Ericson 2012).

The sampling strategy used focuses on identifying different types of land or water use at or near contamination sites, and then collecting composite samples for each major type of land or water use. For example, for soil contamination, land use at or near a site might include a storage yard, two agricultural fields, a woodland, a village and a schoolyard (with "near" typically meaning within several hundred meters). Composite samples would be collected for each of these six areas. For water, a site might have several wells nearby, plus a farm pond and small stream, so composite samples for each of these potentially contaminated locations would be collected. In addition, if locations are observed by the investigator where particularly high concentrations of POPs are suspected, such as a pile of what appears to be pesticide waste, targeted samples would be collected there. In this way, an understanding of the general levels of contamination for each type of land use and pathway near a site is determined, along with some information about potentially very high exposure risks. Incremental sampling is not currently included in the ISS, which instead relies on composite and target samples. Incremental sampling may allow for better site characterization, however it would also require markedly more time, effort and expertise on the part of trainers and investigators, while a simple composite is easier both to explain and collect. Given the scope of the overall effort and relative value of sampling in the REA, the existing ISS methodology was decided to be most appropriate. As such, the sampling matrix from the ISS protocol was integrated exactly into the revised REA.

A second key area of expansion in REA was a simplified means to characterize and document the condition of storage facilities. Criteria from several existing protocols were synthesized into a Containment Type and Quality Matrix. The matrix is essentially a questionnaire to be completed by the investigator, consisting of a series of pull downs lists, free text entry fields and self-populating values. Examples of the type of data collected on sites are the type and condition of storage containers, quantity and types of POPs present or known to be present in the past, site management information, data about past remediation work, and many more. The questions and pull down lists are presented in a way to be understandable to less experienced investigators, and are arranged to lead the evaluator through the evaluation process. When completed, these fields interact to create an overall containment type and quality value that is later incorporated into a risk algorithm to estimate source risk.

The third major expansion of the existing FAO REA was the integration of Geographic Information Systems (GIS) data. Freely available GIS layers were accessed and processed for incorporation into the REA. This information included data regarding population density; streams and other watercourses; general land use; terrain (e.g. mountainous, plains, forests, farm or pasture land); and soil type, among other layers. A key challenge with the integration of GIS into the system was the identification of an appropriate software tool. Concerns about limited local financial and technical capacity to manage complex GIS systems, led to innovative uses of less complicated approaches. In particular, the REA modification provides the ability to put GIS data into an Excel based format, which is commonly available and usable in almost all countries, requiring less cost and expertise than more sophisticated GIS platforms such as ArcGIS.

Revised REA Method for Vietnam

The resulting VEA REA package is composed of two distinct stages, the Desk Screen and the site visit, or REA. The initial prioritization is conducted with the Desk Screen module. High priority sites are then visited by a trained investigator and the REA is carried out. The REA includes risk calculation algorithms that allow the comparison of sites and prioritization for further action. All completed REAs are then stored in an online searchable database. The resulting revised REA package for Vietnam consists of three separate but interactive software products: the Desk Screen, the REA, and the online database.

Desk Screen: The purpose of the Desk Screen is to help users prioritize sites for visits based on limited information. This is considered necessary in Vietnam because there are thousands of sites that could be visited, but even with limited time at each site (1 to 2 days) and limited sampling, there is not sufficient budget or resources to conduct REAs at all sites. In BI's experience, this situation is common to many countries. Developing a method to prioritize visits allows users to more effectively use limited resources. The various values are utilized in an algorithm to determine the "Visit Priority." Three rankings are possible: High, Medium and Low Priority.

In the Desk Screen product, whatever database of currently known contaminated POPs sites is entered into the product. The form is based on Excel, which allows for relatively easy customization of entry from whatever electronic format exists for the available information. At a minimum, a site name and location must be entered, along with some identification of the POPs suspected at the site and hopefully some information on quantity of contaminants. Site latitude and longitude must be entered to assure unique identification of sites and as a basis for addition of GIS data. Then publicly available GIS data is loaded into the product to provide cursory site and area characterization. Specifically, for Vietnam, soil type, population density, land use, altitude, and proximity to a river, all populate based on the latitude and longitude of the site. This GIS information coupled with available site data is processed through an expert algorithm to provide a very general risk classification for use to develop site visit priorities. Information in the Desk Screen can be automatically uploaded in to the REA product to avoid the need for duplicate entry and consistency of site identification. The Desk Screen document represents an innovative method to enter and use GIS data within the Excel environment.

As with the REA template discussed below, the Desk Screen incorporates several preloaded chemical specific values, which populate into the screen and are used in the risk estimate based on which chemical is chosen. These chemical specific values include half-life in soil, sorption coefficient, water solubility and recommended safe environmental levels. To limit file size, relevant layers within ArcGIS were cropped to the boundaries of Vietnam and their resolution limited to 30 arc seconds (~1km). These layers were then exported to ASCII files and further converted to a .csv format, suitable for accessing with Excel. Earlier versions of Excel are commonly used in Vietnam and limit the number of possible rows to 65,536 which inhibits the ability for these files to be saved as .xls or .xlsx.

The Desk Screen document links to the relevant .csv files and executes lookup functions based on the latitudinal and longitudinal coordinates entered. In so doing, the Desk Screen document saves all the values from these .csv files in a non-visible, hidden table (External Link Table). Certain values, such as data from the Harmonized World Soil Database (HWSD) had to be further cross referenced with additional datasets to extract required information. Non-GIS related equations function similarly to the REA template, with key information stored in a hidden tab.

REA Product: The central REA product is a MS Excel-based form for rapid on-site assessment with 4 distinct sections:

1. General Background about the site (e.g. location, ownership, history, etc.);
2. Type and Quantity - identification of pollutants at the source location;
3. Release Risk - risk that POPs were or are being released and migrating to receptors of concern); and
4. Receptor Risk - number of people at risk of exposure and means of uptake, such as ingestion of water, ingestion of food, inhalation or dermal exposure.

These latter three sections correspond to the Source-Pathway-Receptor model for site risk assessment.

The use of this central product is to guide investigators through the site assessment process in the field, using a clear process and simple language. The form presents survey questions and fields in an intuitive easy to use format, with specific questions for the investigator to answer, using pull down menus and a "check the box" approach wherever possible to coach the investigators on the types of things to look for and appropriate answers, as well as to assure consistency in investigation responses. The forms for each section can be completed in the field on a laptop or compatible tablet computer, or can be recorded on paper versions of the forms in the field for later computer entry in the office.

The form was made available in both English and Vietnamese. Users are able to toggle between these two languages with a pull down menu beneath the main navigation panel on the left of each section. Certain values populate automatically based on selections such as the recommended safe environmental levels, soil half-life, sorption coefficient, and water solubility, all populated based on the specified contaminant chemical. Some of these values are then later integrated in the risk ranking algorithm. Once an REA is completed, it can be saved to the user's hard drive and uploaded directly to the online database.

The form was developed in a legacy version of Microsoft Excel to enable full functionality across a range of platforms. Earlier incarnations included macros to maximize ease of use, however these were removed in the final version as macros tend to behave differently across platforms. Equations utilize lookup functions to reference data stored in hidden sheets. Similarly, pull down and survey question text is stored in hidden sheets and retrieved base on the user's actions (e.g. language selection).

In our experience, this rapid assessment process typically requires less than one day at small or moderate sites, and perhaps up to two days for large or complex sites. This includes the time required to collect samples, as discussed above. Based on the information collected and entered into the REA product by the field investigator, along with the GIS data entered centrally and sampling results, the product develops risk scores for the site. Algorithms are embedded in each sheet and utilize the values entered by the user. The algorithms reflect the proximity, type and density of receptors, as well as land and water use near the site, type of exposure (inhalation, ingestion, dermal), and any known soil or hydrogeologic information. The algorithms also utilize the pre-populated chemical specific data. The algorithms used to develop the risk scores were developed through evaluation of several risk estimation models and in consultation with assessment experts so as to incorporate their knowledge and experience.

Specific risk scores are developed for Source, Pathway and Receptor risks, and then are added to form an overall site risk score that can be compared to other sites. As this is a rapid assessment, the results are presented in terms of higher or lower risk, defined as High, Medium and Low Priority, as opposed to a quantified, specific level of risk such as 1/10,000 risk levels, which requires far more evaluation to develop.

Online Database: BI developed an online database for storage and retrieval of completed REAs. Once online, data can be further sorted and queried. The organization of the online database follows that of the Excel-based REA. Several features are worth noting here. The database is password protected and offers different levels of access. A site administrator can limit the access of users by their ability to view and/ or edit province specific information. Similar to the REA template, the online database is available in both English and Vietnamese to accommodate different users. Also similar to the REA, algorithms are embedded and chemical specific values populate automatically.

One key feature of the online database is the integration of a Google Maps interface. All saved sites with latitudinal and longitudinal coordinates automatically appear on a map of the country. The sites are indicated by pins, which can be clicked to access site-specific information.

VEA expressed a desire to be able to access the data in a number of formats. Thus all or some of the information stored in the database can be downloaded to an Excel document. Additionally the database allows for storage of associated files such as photographs and supporting documents. Finally, in addition "Site Profiles" can be printed from the database with responses to all fields. Also in response to VEA requests, all assessments carried out prior to this project were bulk uploaded into the database. The online database resides on an open source Unix platform which runs Apache HTTP Server with data stored in multiple mySQL database tables. All information is accessible via a password protected web interface written in php/html/javascript.

VEA Rapid Assessment Method Development and Testing

Three separate field trials were conducted during the project, during which nine sites were screened. Revisions were made to the REA following each field visit. The initial version of the REA package was developed as an ArcGIS 10 Add-In. The Add-in was composed of a series of sequential forms running on top of the ArcGIS background. The forms asked the user to enter basic site characteristics, such as the name of the site and its longitudinal and latitudinal coordinates. Based on this information the form would run a number of queries of GIS layers and provide the user with certain fields of information about the site, including soil type, slope, and distance to water. Completed sites were stored in a searchable database accessible through the Add-In.

Early demonstrations of the protocol to VEA led BI to shift away from the ArcGIS 10 Add-In. Concerns arose regarding the complex nature of the software and relatively high cost. The BI team was instead encouraged to utilize Microsoft Excel, with which VEA staff were much more accustomed, for the data entry components, and as the base for an online database for storing and querying completed sites. This new direction presented a new set of challenges to the BI team, particularly with regard to the integration of GIS data into the protocol.

In addition to software and organizational adjustments, a handful of other revisions were also made to the protocol following site visits. Foremost among these were changes in the dominant focus on storages of obsolete material. Site visits revealed that at many locations, material had been removed and consolidated elsewhere. In many of these cases, area soil and water remained heavily contaminated. Thus a prioritization method that overly focused on the quantity of material present would likely insufficiently characterize the risk posed by the site. The protocol therefore required adjustments to more accurately capture the chronic, as well as acute (such as catastrophic failure of a site), exposures present.

CONCLUSION

The REA developed by BI is a simple and effective instrument to rapidly and affordably characterize the risk posed by POPs contamination sites. The tool is not overly complicated and sufficiently captures key information about a contaminated site. Available GIS data is incorporated as a useful starting point for site evaluation. Targeted, limited sampling provides a basis for general understanding of receptor risk while also limiting analytical costs. More importantly the protocol can be competently utilized by trained inexpert assessors and typically requires site visits of one day or less, including sampling. Finally, the tool is built on a combination of widely used proprietary (notably Excel) and open source platforms, thus allowing for relatively easy adoption and modification by other country governments.

The health hazards associated with pesticide production, use and disposal are well studied and global in nature. Every country uses these chemical agents and ultimately un-used or expired pesticides need to be disposed of in an environmentally safe manner. However, the experience in Vietnam and other low and middle income countries revealed numerous areas where pesticide disposal was poorly implemented and managed. Traditional environmental site assessments methods can be burdened with the collection of numerous climatic, geological, geographical and of course chemical parameters, including extensive sampling. While detailed comprehensive site assessments are optimal, they are very costly, take a long time and out of reach for most low and middle income countries. The approach presented in this paper simplifies the data collection set and mitigates cost, expertise and time challenges often faced by governments of low and medium income countries as they work to catalogue and prioritize the large number of such areas. However, the rapid assessment process developed is only suitable for gaining a basic understanding of contaminated site risks sufficient for establishing priorities for further evaluation, based on public health and environmental risk. The process is not sufficient for nor intended to serve as a basis for quantitative calculation of risks or development of remediation efforts.

The assessment methodology described above is undergoing additional field-testing in Vietnam with possible expansion into the Former Soviet Union and other regions to better assess its utilization and efficacy. Hopefully, this rapid and cost-effective methodology will prove useful in better understanding the extent of contamination and human health impact associated with improper disposal of POP pesticides.

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REMEDIATION OF POP PESTICIDES POLLUTED AREAS IN THE CONDITIONS OF MOLDOVA

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KEYWORDS
Persistent organic pollutants (POPs), obsolete pesticide (OP), contaminated sites, risk assessment, remediation

ABSTRACT

During the last decade, pollution due to POP pesticides has been recognized by the Moldovan authorities as a problem of national priority which needs to be resolved in order to reduce/eliminate the impact of POPs on human health and the environment. As a result of national inventory carried out in 2008-2010 about 1600 contaminated sites were identified and described.

This study on remediation of POP pesticides polluted areas is complementary to the actions undertaken during last years in the field of sustainable POPs management and has as specific objectives: (i) to identify Best Available Technologies (BAT) for of POP pesticides polluted areas, taking into account technical, financial and economic aspects; (ii) to assess their potential environmental/health benefits and impacts; (iii) to implement appropriate remediation techniques at a few selected sites.

Based on the assessment which included aspects of practical and economic feasibility for implementation taking into account costs, performance, efficiency and potential impacts on the environment and human health, two techniques – isolation in controlled soil stockpiles and biological treatment with the Daramend technique have been selected and tested/validated at three pilot demonstration sites in order to identify methods most appropriate for Moldova with a view to recommendation of remediation strategies for other OP sites throughout the country pending the available financial resources.

Based on practical results the Guidelines for local environmental authorities on how and when to carry out remediation measures on areas polluted with POP obsolete pesticides have been prepared.

INTRODUCTION

By the early 1990s, about 1000 warehouses for pesticide storage had been built in the collective farms. During the period from 1991 to 2003, most warehouses were destroyed or dismantled and only about 20% were maintained in a satisfactory condition. Significant amounts of obsolete pesticides were stored in the open inadequate containers and areas adjacent to warehouses were contaminated as a result of improper management of OP storage. As some storage facilities are situated close to residential areas and water courses, the risk of harmful effects on the environment and people's health is thereby greatly increased.

In November 2003, the Moldovan authorities began repackaging and transportation of obsolete pesticide stockpiles scattered across the country to a limited number of warehouses. Upon the finalization of these activities in 2008, about 340 warehouses have been fully emptied from obsolete pesticides, ensuring the elimination of the most direct threats to human health and the environment. At the same time, emptied warehouses remain a significant pollution source because their walls, floors, and adjacent territories are contaminated.

Tackling this problem require a detailed inventory and risk assessment of those sites, along with development of appropriate remediation measures. Such studies were conducted in parallel in 2008-2010 by the Ministry of Environment within two projects supported by the World Bank. As a result of the first study about 1600 contaminated sites were identified, described and included in an integrated database: http://pops.mediu.gov.md.

The second study, presented below, was carried out to satisfy the urgent need for selecting suitable and affordable technical options for clean-up of obsolete pesticide residues and remediation of contaminated sites. It was conducted within the CIDA/WB Project "Remediation of POP pesticide polluted areas and inventory of PCB contaminated oil in power equipment" by the NIRAS Consulting Engineers and Planners A/S, and managed by POPs Sustainable Management Office (www.moldovapops.md).

The specific objectives of this study were:

- to identify Best Available Technologies (BAT) for of POPs pesticides polluted areas, taking into account technical, financial and economic aspects;
- to assess their potential environmental/health benefits and impacts;
- to implement appropriate remediation techniques at a few selected sites.

The remediation techniques had to be tailored to best fit local characteristics like soil type, hydrogeology, contamination degree, and pesticide category. The identified techniques had to be tested/validated at selected pilot demonstration sites in order to identify methods most appropriate for Moldova with a view to recommendation of remediation strategies for other OP sites throughout the country pending the available financial resources.

1. CLASSIFICATION OF POP PESTICIDES POLLUTED SITES

During the initial project phase, data collection to identify site characteristics was initiated. Criteria for pre-selection and final selection of three demonstration sites to test remediation technologies were defined. For data collection, an Access database was designed and all available at that moment relevant data/information for 386 OP sites was recorded in the database.

The matrix criteria used in the database for pre-selection of sites were defined and identification of different groups of site was based on the following considerations:

- Site conditions affecting choice of remediation technique:
    - contamination level (buildings and soil and water if underground water at the depth of few meters),
    - expected extent and location of soil pollution,
    - soil characteristics,
    - present land use with respect to remediation (agricultural, industrial or residential use of land),
    - need quick solution – isolation techniques (waste depository) to remove soil contamination and contaminated rubble and waste,
    - no future security for isolation techniques and site is available with respect to time and space to do biological treatment,
    - site to be used in the future / not to be used in the future and is the site fenced or guarded.
- The need for remediation i.e. risk to human health and environment:
    - contamination level,
    - the proximity of OP sites to the residential or industrial areas (any sites with permanent human residence) and the number of affected persons,
    - the proximity to the source of drinking water (shallow wells, deep wells of central water supply intakes),
    - the proximity to the surface water (especially recreational zones or water body used for fish farming) and the depth of the groundwater,
    - the proximity to the agricultural land, pasture and livestock,
    - proximity of all kind of protected nature areas and ecosystems,
    - landscape features such as the down/uphill location of sensitive targets with respect to location of the former warehouse, degree of soil erosion, predominant wind direction, etc. are also parameters that can be used to assess the need for remediation.

Based on the data available concerning the former OP warehouse, the main criteria for classifying the sites has been as follows:

1. Soil pollution levels and potential for pollution in floors and walls. The threshold for soil is the National Standard for soil pollution for HCH (Hydrocyclohexane) (0.1 ppm) and DDT (0.1 ppm);
2. State of repair of the warehouse – integrity of walls, roof, door and windows determining the containment capacity of the building;
3. Threat to human health dependent on the proximity to sensitive human and ecological targets;
4. Type of soil under and around the warehouse classified either as permeable to rain water, i.e. leaching to groundwater can occur or low permeable soils with a low leaching potential.

Of the 386 records for former OP warehouses, only 96 records contained information which could be used for classification of the sites according to criteria 2 and 3 mentioned above. When all 4 criteria were applied, only 40 records were selected (meaning only these 40 sites have the necessary information on soil pollution, state of repair of the warehouses and factors determining the threat for human health and soil type).

For further assessment, a top 10 list of OP sites was derived and the priority criterion for selection was the available information on the soil pollution. Evaluation of the top 10 sites and final selection of three demonstration sites was done after an in-depth analysis and supplementary site investigation.

2. EVALUATION OF APPROPRIATE BATs FOR REMEDIATION

The applicability of BAT Remediation Technologies for clean-up of sites polluted with pesticides (contaminated soil) was identified and assessed. The assessment included aspects such as practical and economic feasibility for implementation in Moldova and took into account costs, performance and efficiency as well as treatment time in full-scale field trials; and potential impacts on the environment and human health.

Risk Management

Present day state of art remediation projects usually use a combination of techniques in order to optimize the remediation process and ensure that risk to human, ecological or environment targets are reduced as much as possible and that site specific clean-up goals are achieved.

The risk management concept for remedial options is based on ability of different kinds of remedial options to prevent risks in relation to the conceptual model describing the source of contamination and spreading to the environment and human targets.

The most evident solution is the removal of the primary pollution source which often involves excavation of waste and contaminated soil. The chemical waste and contaminated building rubble and soil requires treatment which is usually provided in off-site treatment plants. At very large sites with a large volume of soil and waste, mobile treatment plants can sometimes be economically viable.

Other remedial solutions can prevent the release of the pollutants to the environment by encapsulation etc., but for many “old” sites widespread contamination has already occurred and various remedies need to be applied to different media; soil, groundwater, surface water, soil air.

Another way to approach the problem of contamination is to prevent exposure of sensitive targets. This approach can be administrative by restricting land use combined with site specific and land-use related clean-up targets or merely prevent the most significant exposure routes. For the former OP warehouses, the most significant exposure route is by direct soil contact and spreading by soil erosion and runoff. This is illustrated in Fig. 1.

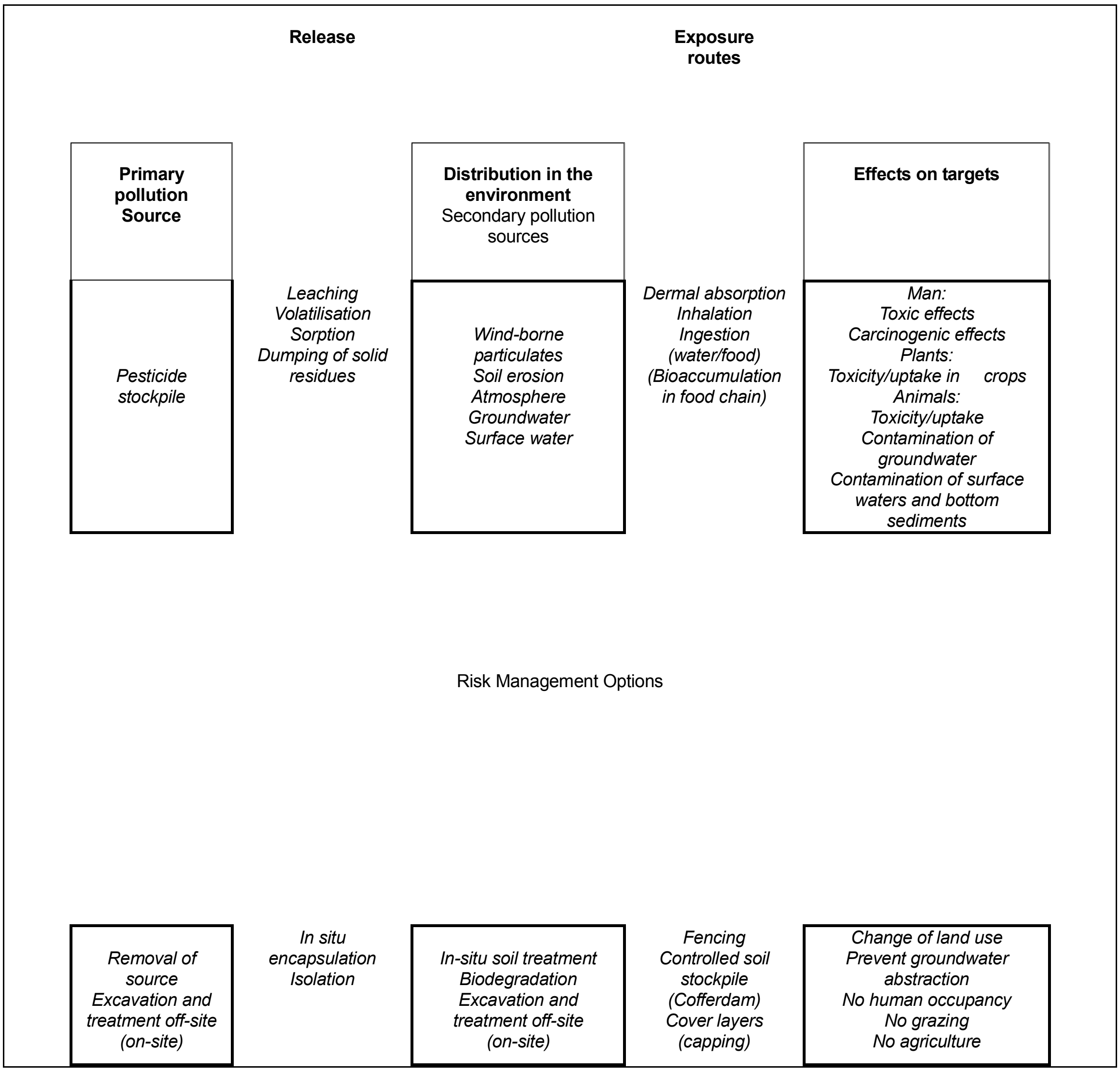

Fig. 1. Risk management options preventing release of contamination and exposure routes

Identification of available techniques

There are many literature reports on potential techniques to clean-up soil contaminated by pesticides and persistent organic pollutants (POPs). Most of the information on BAT and performance data for techniques using biological and/or physical-chemical methods and in-situ remediation is found in treatment technology reports from US EPA /1/ and NATO/CCMS /2/. Furthermore, reports considering promising technologies and for use in developing countries, i.e. without high temperature incineration facilities have been prepared under UNEP /3, 4/.
All selected BATs should already be tested and approved by international organizations (Secretariat of the Basel Convention, UNEP, UNIDO) and/or by relevant national authorities in other countries (e.g. US EPA). Furthermore, the selected BATs should not have adverse impacts on human health and the environment.
The identification of suitable techniques for the clean-up of POP pesticide contamination at OP sites in Moldova was based on consideration of the following aspects:

- soil contaminants,
- characteristics for soil pollution at former pesticide warehouse storage sites,
- objectives for clean-up,
- practical and physical restrictions for implementation,
- economics,
- performance and efficiency,
- time-frame and need for post clean-up monitoring etc.,
- environmental effects.

The evaluation of existing data on stockpiles of pesticides at warehouses and the few analyses of soil samples at some of these sites indicate that the main contaminants of interest are DDT, Lindane (gamma-HCH) and possibly hexachlorobenzene (HCB) and Heptachlor. Other POP pesticides such as Aldrin, Chlordane, Dieldrin, Eldrin, Chlordecone, Hexabromobiphenyl, Mirex and Toxaphene are not expected in high concentrations as these have not been detected in soil samples during previous studies. The selection of relevant clean-up techniques was based on the ability to treat chlorinated pollutants such as DDT, Lindane (HCH), HCB and Heptachlor.
The following guiding principles have been followed while selecting the clean-up techniques to be recommended.
Economics: For most of the technologically sophisticated techniques, treatment costs per tone of contaminated soil are lowest if large soil volumes are to be treated. Likewise, the most mobile treatment plants are economically feasible with high volumes of contaminated soil (total volumes of between 50,000 – 100,000 m^3). However, the volumes of contaminated soil at most warehouses are expected to be less than 1.000 m^3, i.e. an area of 45x45 m^2 and soil pollution to 0.5 m in depth. The selection of relevant clean-up techniques is therefore based on techniques that are low cost, also for low volumes of soil to be treated.
Performance and efficiency: It is important that the selected technique is not sensitive to variation in the type and nature of the contamination or require many fine adjustments of the process in order to achieve the required effect. The process performance must be efficient, reliable, and consistent and be able to reduce contamination level to the required clean-up level. Many techniques report clean-up performance of up to 99.99 %, but if the initial concentrations are >2%, then the final concentration is >2 mg/kg. The selection of relevant clean-up techniques is therefore based on robust and reliable techniques.
Time-frame and need for post clean-up monitoring: It is important that the selected technique can complete clean-up to the required criteria within a reasonably time frame. It is also desirable that there are no long-term requirements to monitor clean-up levels or control integrity of clean-up measures e.g. if using containment measures.
Environmental effects: It is important that the selected technique does not produce residues, wastewater and gaseous emissions that can contaminate the environment and requiring special treatment. Other environmental aspects such as high energy and water consumption, noise, use of raw materials, limitation of access or utilization of land must also be reduced as much as reasonably possible.

Recommended BAT demonstration projects for Moldova

Two remediation (BAT) techniques have been chosen for the three demonstration sites with a view to possible further implementation in Moldova.

Enhanced Bioremediation

These techniques usually involved mixing of the soil with additives to promote anaerobic conditions (zerovalent iron, hydrocarbons such as starch) and nutrients to enhance biological degradation.
The Daramend technique involves sequential cycles of anaerobic (no oxygen, strongly reducing conditions) and aerobic (oxygen present) conditions. The anaerobic conditions are generated by mixing with the Daramend

additive (zerovalent iron or zinc and an organic component to stimulate microbiological growth) and the application of water to maintain optimal moisture levels. After a period of 1-2 weeks with anaerobic conditions, dechlorination of the organochlorine containing pesticides is initiated. The dechlorinated products are then removed by soil bacteria under aerobic conditions generated by tilling (ploughing) of the soil. It has been applied in-situ or by preparation of on-site degradation cells as documented by a number of reports /5, 6/. The Daramend treatment will not prevent using the soil for agricultural purposes after clean-up, although adjustment of pH by chalk addition might be necessary. The process is patented by Adventus and the company is prepared to guarantee the remedial performance of the technique. The typical depth of treatment is 60 cm if using a deep rotary tiller /5/.

At one full-scale treatment site /1/, the Daramend technique reduced level of DDT by about 90 %. At another site with low-level DDT levels, concentrations were reduced by 65-84 % within 3 weeks /5/. Levels of lindane are also reported reduced from 13 mg/kg to 0.28 mg/kg after 103 days of treatment.

Isolation in controlled soil stockpiles

Soil contamination with immobile contaminants can also be managed by containment. The construction of a controlled soil stockpile (cofferdam) ensures that the soil is removed and isolated with protective top and bottom liners.

Isolation and management techniques cannot be considered as "permanent solutions" since the soil is still contaminated and the main disadvantage with this approach is that it is difficult to ensure that no future activities are carried out involving destruction of the cofferdam unless the end use of the site is restricted.

The controlled soil stockpile (cofferdam) will be fenced and equipped with warning signs, although this provides no guarantee to prevent future misuse. The integrity of the fence and cover layers of the soil stockpile need to be inspected regularly to ensure that no loss of structure integrity occurs to avoid unintentional contact and spreading of soil pollution in future.

Alternatively, the contaminated soil from several sites could be collected and isolated in a controlled soil stockpile at municipal waste sites operated by the local municipal authorities and subject to environmental controls.

The major advantages with this solution are: i) the contamination will be removed so that no exposure to sensitive target can occur; ii) it is a proven technique and efficient; iii) it is simple and cheap and therefore can be realistic implemented by local authorities in Moldova at all kinds of site.

An alternative or supplement to the establishment of a controlled soil stockpile could be the establishment of hard cover layers over the soil contamination. This solution has more or less the same advantages and disadvantages as for the cofferdam as it is not a "permanent solution".

As it is important to improve the current situation and protect the people living close to the polluted areas and prevent further spreading of POPs to the environment, it was recommended to demonstrate implementation of isolation and management techniques at the former OP warehouse sites as these are well proven, quick and efficient techniques. Furthermore, testing and implementation of biological treatment in a demonstration project at one of the sites was recommended.

Selection of remediation techniques

The two techniques that are recommended for testing in demonstration projects as appropriate remediation techniques for former OP pesticide warehouse stockpiles are therefore:

- Controlled soil stockpile (Cofferdam),
- Biological treatment with the Daramend technique at one site.

These techniques have been selected with respect to cost and an evaluation of their ability to be applied by local authorities at former OP warehouses. The Daramend technique is however not documented to a clean-up criteria of 0.1 mg /kg as previous remediation projects have included sites with high levels of pesticides and high acceptance criteria. The technique was however assessed to be promising. Therefore this technique should be seen as a demonstration case and future implementation at other sites in Moldova depends on the type of site and the clean up criteria for the site in question.

Other assessed techniques such as thermal treatment, which require process equipment in fixed or mobile units and high-level power supplies, or dechlorination, which often involve several stages with both thermal and chemical treatment also requiring process equipment in fixed or mobile units and high-level power, and water supplies, are expensive and usually cost-effective only for large volumes of contaminated soil or waste. Therefore they were generally not considered applicable in Moldova for on-site treatment of diffuse or low-level residual soil pollution at former op warehouse stockpiles.

3. SELECTION OF DEMONSTRATION SITES

Finally, based on above mentioned criteria, three contaminated sites for demonstration have been selected and proposed clean-up actions for each particular site as well as approximately amounts of soil to be treated are:

- Bujor – combination of bioremediation and isolation in cofferdam of demolished foundation. Amounts: bioremediation – 170 tons soil, cofferdam – 340 m³ soil, demolition wastes – 449 m³. Excavation and backfill the site with clean soil – 550 m³. Cofferdam built on site.
- Congaz – demolition of building and cofferdam with both soil and demolition waste. Amounts: soil – 780 m³; demolition waste – 1030 m³. Excavation and backfill the site with clean soil – 1020 m³. Cofferdam built 3 km south-west off site.
- Step-Soci – demolition of foundation and cofferdam with both soil and demolition waste. Amounts: contaminated soil – 30 m³; demolition waste – 120 m³. Excavation and backfill the site with clean soil – 150 m³. Cofferdam built on site.

4. REMEDIATION AT THE DEMONSTARTION SITES

Remediation activities at the demonstration site works have been preceded by a preparation process involving the development of the documentation legally required before starting the works - Work Program for Cofferdam and Work Program Bio-remediation. Also, it was necessary to develop the so-called Technical Design of Works. According to Moldovan legislation, this document must be developed by authorized engineers, and should pass a process of approval in order to receive the required works permits.

Controlled soil stockpile (cofferdam)

The scheme illustrating principle construction of a cofferdam is shown in Fig. 2.

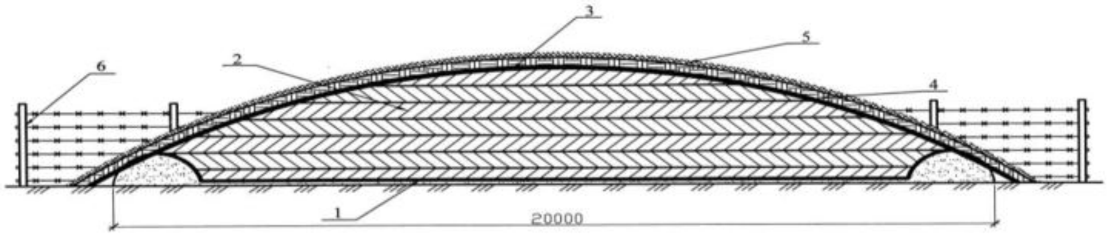

fig. 1.2 Schema constructiva a depozitului de deseuri contaminate cu compusi organici persistenti
1 - pelicula de polietilena de acoperire a patului depozitului (membrana inferioara)
2 - pamint si moloz contaminat asezat in straturi si compactat
3 - pelicula de polietilena de acoperire a depozitului (membrana superioara)
4 - strat de sol fertil
5 - iarba semanata
6 - ingradire depozit, realizat din stilpi si sirma ghimpata (plasa)

Fig. 2. Constructive scheme of controlled POPs contaminated soil stockpile (cofferdam): 1 - polyethylene film covering the bed of cofferdam (buttom membrane), 2 - contaminated soil and rubble placed in layers and compacted, 3 - polyethylene film covering cofferdam (top membrane), 4 - layer of topsoil, 5 - sown grass, 6 - fence made of concrete pillars and barbed wire (mesh).

The cofferdam is a *constructed controlled pile* where contamination from the content stored inside it (in our case - contaminated soil and contaminated demolition wastes) to the ground water is secured by a *bottom and top liner (membrane)* and the soil is secured against surface water and rainwater by a *bank around the pile* and a *top liner*. The top liner is secured with a layer of clean soil topped with grass and a fence with warning signs are placed around the cofferdam.

The piles should be constructed with a small 50 cm high bank and be covered by a double HDPE liner. The excavated soil and demolition wastes are stored on top of this bottom liner. The main purpose of the bottom liner is to indicate the border between clean and contaminated soil. The soil surface is formed in the shape of a pyramid or roof and covered by a double layer of HDPE liner. This double roof liner is secured against wind and rains by a layer of clean soil. The roof liner should be mounted ongoing as building up the pile also securing the pile against rainwater through the night.

Since the main function of a cofferdam is isolation the requirements toward this kind of construction consist of respecting/considering a number of factors which could affect its function/purpose:

The right topographical location – the cofferdam should be located in an area where there are no risks of land slides, earthquake trigging a landslide, heavy run-off (slope of the terrain), flooding. These are the geo-climatic factors able to destroy the whole construction if not taken into consideration while selecting the spot where cofferdam is going to be built;

The right design and its diligent execution in order for the cofferdam to face the extreme manifestation of the meteorological factor: heavy rain/wind, snow pressure. These are meteorological factors which can damage the integrity of the cofferdam if not considered by designers and builders during the works;

The content of the cofferdam should not consist of big sharp parts of demolition wastes able to damage/rip the isolation material (liners) or these should be safely stored in the middle of the pile and not consist of construction materials which could be directly reused by population;

The access to cofferdam is denied – fences and warning signs are mandatory steps in cofferdam constructions.

Bioremediation – DARAMEND for organochlorine pesticides in soil

DARAMEND is an advanced biological treatment technology for soil, sediment and solid wastes contaminated with recalcitrant organic compounds /3/.

The bioremediation test at the Bujor site included 10 cycles of Daramend application. The total surface of the test area was about 200 m^2. The depth of tilling was 25-30 cm. The results of HCH, DDT and Heptaclor concentration in the soil for the baseline analyses and after 5 as well as after 10 cycles of treatment are compared in the Tab. 1.

Tab. 1. Mean concentration in treatment and control areas before and after treatment with 5 and 10 cycles of Daramend treatment respectively

	Area 1	Area 2	Area 3	Area 4	Area 5	Control area
Sum of HCH	mg/kg dw (mean values)					
Baseline before Daramend treatment	8.7	11.6	50.9	0.25	11.9	56.1
5 cycles Daramend	5.1	8.4	26	0.53	9.4	65.3
10 cycles Daramend	5.2	14	25	0.57	3.7	9.2
% reduction after 5 cycles of Daramend	41%	28%	49%	-	21%	-
% reduction after 10 cycles of Daramend	40%	-	50%	-	68%	85%
Sum of DDT	mg/kg dw (mean values)					
Baseline before Daramend treatment	35.9	10.5	12.9	0.57	22.8	1.5
5 cycles Daramend	12.7	2.2	5.5	1.3	13.5	0.99
10 cycles Daramend	6.6	0.48	1.4	0.22	4.5	0.99
% reduction after 5 cycles of Daramend	65%	79%	57%	-	41%	34%
% reduction after 10 cycles of Daramend	82%	95%	89%	61%	80%	34%
Heptachlor	mg/kg dw (mean values)					
Baseline before Daramend treatment	3.9	0.50	24.7	0.07	2.2	0.06
5 cycles Daramend	0.49	0.49	4.6	0.35	2.73	0.60
10 cycles Daramend	2.3	0.14	4.5	0.13	0.54	0,04
% reduction after 5 cycles of Daramend	87%	2%	81%	-	-	-
% reduction after 10 cycles of Daramend	41%	72%	82%	-	75%	-

As can be seen, the pesticide distributions are not correlated as the highest concentrations of HCH are seen in the control area and area 3, while the highest concentrations of DDT are seen in area 1 and 5. Heptachlor is found in area 3.

After 5 cycles of treatment, appreciable reduction of the content of HCH and DDT are seen in areas 1, 2, 3 and 5, and for Heptachlor in area 3. As the mean concentrations after 5 cycles of treatment were still well above the Moldovan soil quality criterion of 0.1 mg/kg, it was proposed that soil treatment in all areas be extended to 10 cycles of treatment. After 10 cycles of treatment, further reduction of the content of DDT is seen in all areas, but the mean concentrations still exceed the Moldovan soil quality criterion of 0.1 mg/kg. However, no significant reduction between the 5 and 10 cycles is seen for Heptachlor and HCH, except for an apparent reduction for HCH in the control area. In area 4 and the control area the overall contamination level with DDT and Heptachlor is low.

The results after 10 cycles of treatment demonstrate appreciable reduction of up to 84% for sum of DDT, 42% for sum of HCH and 76% of Heptachlor.

The soil contamination is still above the Moldovan soil quality criteria for agricultural land, but the risks associated with contaminated soil have been greatly reduced. The contaminated area at Bujor will not be used for agricultural or residential land use and the residual contamination is less than soil quality criteria for industrial land as defined in some EU countries. Furthermore, the site is usually covered by fairly dense vegetation which prevents spreading of the low-level contamination in soil dust. No further actions are therefore recommended.

5. ECONOMIC EVALUATION

The economic evaluation of the BAT applicability – the direct and total costs as well as the unit price (efficiency) of both methods achieved during the remediation activities are presented in the Tab.2.

Tab. 2. Comparison of Economic Aspects

		Congaz	Bujor cofferdam	Step-Soci	Bujor bioremediation
Amounts of soil and rubble treated,	m^3	4 942	1 545	440	98
Time to achieve cleanup	Day	23	10	8	>70
Man hours required to complete	hr	864	264	126	120
Training hours need to complete	hr	2	2	2	2
Cost of treatment/materials	Leis	39 212	20 662	7 892	112 612
Cost of hire for equipment	Leis	170 450	76 650	26 600	44 246
Cost of manpower	Leis	19 440	5 940	2 835	1 950
Daily Rate, manpower , man/days	Leis	150	150	150	130
Costs of hire equiprment, average	Leis	350	350	350	350
Direct costs	Leis	229 102	103 252	37 327	158 808
Total cost including taxes	Leis	408 297	196 964	71 307	158 808
Cost of PPE		21 419	11 953	5 380	2 767
TOTAL GENERAL		429 716	208 917	76 687	161 575
Price/ m^3	Lei/m^3	86,9	135,2	174,3	1 648,7
Achievement of clean-up goal		100%	100%	100%	50%
Need for maintenance		Yes	Yes	Yes	No
Need for follow up treatment		No	No	No	No
Applicability at other sites		Applicable	Applicable	Applicable	Applicable
Future maintenance		Needed	Needed	Needed	No
Need for future treatment		Yes	Yes	Yes	No
Future cost , treatment		Unknown	Unknown	Unknown	None

6. LESSONS LEARNED

Lessons learned concerning appropriate remediation techniques that can be implemented by local authorities in Moldova can be summarized as follows:

Priority for clean up activities: Risks should be reduced immediately as a top priority if there is risk to human health due to close proximity of the OP site to residential areas or vulnerable drinking water wells, and if the soil pollution and/or contaminated building materials are present at the OP site.

Good detailed site investigations: The site investigation is the basis for decisions on the need for remediation and on the extent of remediation required. Uncertainty as to the extent of soil to be excavated and of the volume of rubble as well as the possible presence of “hidden” structures covered by topsoil need to be minimized or else the waste capacity stated in the design of works and permit can too low. In this case, a new application for a permit might be required causing delays to the implementation and extra costs.

Start planning in good time: The planning process takes time and implementation is not possible in the winter months.

Getting Works Permit: The demonstration projects experienced a number of delays due to the need for clarification on a number of legislative aspects concerning permits to start the work. Some of these problems are solved by the descriptions provided in the guidelines and the template for the Technical Design of Works used for the demonstration projects. It took more than 8 months to obtain the work permits to start the cofferdam works and 3 months to import the bio-remediation agent to Moldova.

The lesson learned is that a simple procedure for approval of remediation of contaminated sites using the controlled stockpile method (cofferdams) routine must be implemented. If this is not the case, it will be very difficult to motivate the “site owners” (local authorities) to implement any remediation actions.

Establish a local advisory facility: From the workshops and dissemination seminar, it is learned that the “site owners” needs a back up advisory facility from e.g. the PMT office or a local consultant attached to the PMT office. The Guidelines should be used by the “site owners”, but anyhow some backup advisory is needed especially in the first remediation projects regarding; site investigations, planning, work permits, use of PPE and training of site supervision managers etc.

Use of PPE: Occupation health aspects involving use of Personal Protective Equipment (PPE) are easier to enforce if a short-term intensive construction project is initiated immediately after training in the use of PPE.

Recommended remediation method is a controlled soil stockpile (cofferdam): As many sites have both contaminated soil and building rubble, the method of choice is to excavate the contaminated soil and rubble to a controlled soil stockpile (Cofferdam). However this method is not a permanent method since the contamination is not treated, but isolated. Risks to human health are prevented, but maintenance is required to ensure the integrity of the protective isolation measures.

If there are a number of smaller sites, there might be economical and management advantages to excavate the soil and waste materials and transport these to a local controlled soil stockpile site, so that maintenance costs can be reduced**.**

Enhanced biological degradation is not directly applicable: The biological method by land farming whereby excavation is avoided is assessed not to be directly applicable in Moldova at former OP warehouses due to uncertainty about the clean up levels that can be achieved for the investment involved and due to the presence of contaminated rubble. Permanent reduction of risk is however achieved, and the land is most probably suitable for industrial purposes especially if combined with an addition step to cover residual soil pollution with a clean soil layer.

If there are a number of smaller sites, there might be economical and management advantages to excavate the soil and transport to a site where biological methods could be implemented using either land farming or bio-piles. The time-scale for treatment could be extended over a number of years and the soil after treatment could be used for non-sensitive land use.

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BIOSTIMULATION AND BIOAUGMENTATION – TWO PROSPECTIVE STRATEGIES OF ADVANCED BIOREMEDIATION TECHNOLOGIES

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KEY WORDS
Bioaugmentation, bioremediation, biostimulation, polychlorinated biphenyls, sediments

ABSTRACT

In the recent decades, several hundred tons of polychlorinated biphenyls (PCBs) have been released into the environment. Due to their hydrophobic properties, PCBs tend to be adsorbed by natural organic matter in the aqueous bottom sediments. Sediment is an essential, integral part of the hydrological system. However, because sediments are the ultimate reservoir for the numerous chemical contaminants, they have the potential to pose ecological and human health risks. Environmental and economic reasons have urged the development of bioremediation technologies for PCB removal from the contaminated areas. One of the methods of their removal is bioaugmentation, defined as a technique for improvement of the degradative capacity of contaminated areas by introduction of specific competent microorganisms to the indigenous population. Another one is biostimulation, defined as addition of nutrients or electron acceptors to improve biodegradation capacity of indigenous microflora. This contribution is focused on biodegradation of PCBs in contaminated sediments using perspective and prospective biostimulation and bioaugmentation approaches of bioremediation. Determination of ecotoxicity of PCB-contaminated sediments represents an important part of our research together with isolation and identification of eleven well adapted PCB-degrading bacterial strains using 16sRNA method from long-term PCB-contaminated sediments sampled from the surroundings of the former PCB factory. Biodegradation of PCBs was performed in the real contaminated sediments with addition of inducers and/or bacterial strains. The obtained results indicated beneficial effect of both biostimulation and bioaugmentation approaches on biodegradation of PCBs, mainly the first one. Data obtained using real PCB-contaminated sediment might be useful in the preliminary design of a site-specific bioremediation strategy.

INTRODUCTION

The widespread use of dangerous, toxic anthropogenic compounds and a long history of poor disposal practices led to pollution of the natural environment and created an urgent need for remediation technologies. In many cases, biological approach to remediation of the polluted environment provides significant advantages over alternative technologies. Most notably, bioremediation can facilitate the complete destruction of hazardous chemicals mostly without generating toxic emission or by-products. Some remediation technologies are mainly used at strongly contaminated locations. However, predominant part of agricultural soil or sediments is not extremely contaminated. Bioremediation technologies therefore represent a prospective ecological and economical alternative of physico-chemical methods of pollutants elimination at the above mentioned contaminated areas. Biological techniques are based on biodegradation of pollutants using degradation ability of the microorganisms, predominantly bacteria or fungi.

A hierarchy of *in situ* treatment approaches has been developed to address different contaminant types, site-specific conditions, and regulatory factors. Natural attenuation, biostimulation, and bioaugmentation are the three accepted practices for enhancing bioremediation. Bioaugmentation can be defined as the technique for improvement of the capacity of a contaminated matrix (soil or sediment) to remove pollution by the introduction of specific competent strains or consortia of microorganisms. Bioaugmentation is used when the competent degradative natural microbial population is not present among the indigenous population or, when population is sufficient, to increase the rate of degradation and shorten the time frame for full scale remediation [1]. Several tools have been developed to increase persistence and the activity of exogenous microorganisms or genes after their introduction into the polluted environment. Bioremediation, involving bioaugmentation and/or biostimulation being an economical and eco-friendly approach, has emerged as the most advantageous soil, sediment, and water clean-up technique for contaminated sites containing heavy metal and/or organic pollutants. Addition of pre-grown microbial cultures to enhance the degradation of unwanted compounds (bioaugmentation) and/or injection of nutrients and other supplementary components to the native microbial population to induce propagation at a hastened rate (biostimulation), are the most common approaches for *in situ* bioremediation of accidental spills and chronically contaminated sites worldwide. However, it should be mentioned that bioaugmentation remains debatable as a scientific and as a technological endeavour [2]. Despite many reports that demonstrate the usefulness of bioaugmentation, and field application [3, 4] there are also cases in which it has failed [5]. The current bioremediation approaches suffer from a number of limitations which include the poor capabilities of microbial communities in the field, or lesser bioavailability of contaminants on spatial and temporal scales. Moreover, many factors like strain selection, microbial ecology, type of contaminant, environmental constraints, as well as procedures of culture introduction may lead to their failure [6]. These drawbacks have opened a gap between laboratory trials and on-field application.

The "soil activation", a concept which is based on the cultivation of biomass from a fraction of a contaminated soil and the subsequent use as an inoculum for bioaugmentation was attempted by [7]. Pre-adaptation of catabolic bacteria to the target environment, prior to inoculation, improves survival, persistence, and degradative activities, leading to enhanced remediation. To improve efficiency of bioaugmentation, microorganisms of different divisions can also be brought together [8, 9]. A successful strategy for *in situ* bioremediation can be the combination, in a single bacterial strain or in a syntrophic bacterial consortium, of different degrading abilities with genetic traits that provide selective advantages in a given environment [10]. Under laboratory conditions (in microcosms) the genetically engineered bacteria and catabolic elements (plasmids etc.) were also tested with positive effects on biodegradation of pollutants [11, 12]. The present strain selection procedures dwell on isolating "super bugs" with high resilience to environmental stresses, those harboring catabolically superior enzymes, and those species that are not human pathogens [13, 14].

As with biostimulation, bioaugmentation can be combined with other technologies to improve effectiveness of pollutant degradation. Improved knowledge on the specific effects of enhancement methodologies and on the toxicological profiles of metabolites produced by indigenous or exogenous microorganisms will further increase the extent of application and acceptance of biological approaches of remediation.

Slovakia belonged to the eight largest world producers of commercial mixtures of PCBs produced under the brand names Delor, Delotherm, and Hydelor. In the locality of the former PCB producer Chemko Strážske, a big amount of these substances is still persisting in sediments and soils. PCBs were manufactured mainly in the 1960s and 1970s. From 1959 to 1984, production of PCBs in Slovakia was approximately 21,500 tons. About 46% of the PCB production was exported mainly to the former East Germany. The rest (11,613 t) was used in the territory of former Czechoslovakia in dielectric fluids for transformers and power capacitors, as heat exchanger and hydraulic fluids, as paint additives, and lubricants. Nowadays, the use of PCB formulations in open systems is not allowed in Slovakia however, in closed systems such as transformers and capacitors, they still can be used. It is estimated that about 1,600 tons of PCB wastes were generated during the production, 1,000 tons are in closed systems (transformers, capacitors, and other equipment), 1,500 tons in various wastes and 900 tons in waste dump Pláne. Contamination at the factory Chemko Strážske surroundings belongs to the so-called "old environmental burdens". It directly relates to the former PCB production. Contaminated areas are found inside the factory area as well as in wider surroundings. The contamination is primarily spread through surface water by gradual release from contaminated bottom sediments of an open sewer that leads from the factory to Laborec River, and subsequently through the inlet canal leads to the water reservoir – Zemplínska Šírava Lake. A thin layer of mud in the 5.3 km long effluent canal of the former PCB producer still contains about 3 kg PCBs in 1 ton of dry effluent canal mud 15 years after the termination of the production, and thus represents a serious environmental threat by PCBs. This sediment is an abundant PCB source causing the long-term contamination of the waters of Eastern Slovakia. As expected, the highest value was found in a muddy part of the effluent canal flowing from the Chemko factory (one of the samples contained up to 5 $g.kg^{-1}$). It is doubtless that the polluted effluent canal emptying into the Laborec River has caused the contamination. The Zemplínska Šírava water reservoir (33.5 km^2 surface area) that is partly filled from the Laborec River contained several hundred times higher PCB levels (100 - 2000 times) in comparison to a similar water reservoir (Domaša) in the background area (1.7 - 3.1 $mg.kg^{-1}$ compared to 0.007 - 0.01 $mg.kg^{-1}$) [15].

The remediation of contaminated sediment is becoming more common throughout the world. Ongoing remediation projects can be found in many countries. Technologies including capping, monitored natural recovery, and dredging have advanced and continue to develop. It seems reasonable to speculate that the number of countries with regulatory frameworks for management of contaminated sediment will continue to expand as concerns about the risk of contaminated sediment and debate about the best approaches to remediation continue to mount (Spadaro, 2011) [16].

MATERIALS AND METHODS

Microorganisms

The isolate from long-term PCB contaminated soil *Pseudomonas stutzeri* [17], purified, identified, and maintained as safe keeping in the Czech Collection of Microorganisms (Masaryk University, Brno, Czech Republic) was used for the purpose of bioaugmentation. The other isolates from long-term PCB contaminated sediments *Ochrobactrum anthropi, Pseudomonas mandelii, Starkeya novella,* and *Achrobactrum xylosoxidans* [18] were used for bioaugmentation as well (results not shown). In the strain *P. stutzeri bphA* gene was detected [19].

Sediment Sampling
Sediment sampling protocol was in agreement with the technical norm ISO 5667-12:2001. The sediment corer sampler (UWITEC Corp., Austria) (Fig. 1) was used as a sampling device. The sampler used is a transparent plastic tube that allows for visual examination and sample partition into several layers. Studied sediments long-term contaminated with PCBs were sampled from industrial Strážsky canal that flows into the water reservoir and represents abundant source of contamination.

Fig. 1. Sediment sampling device (UWITEC).

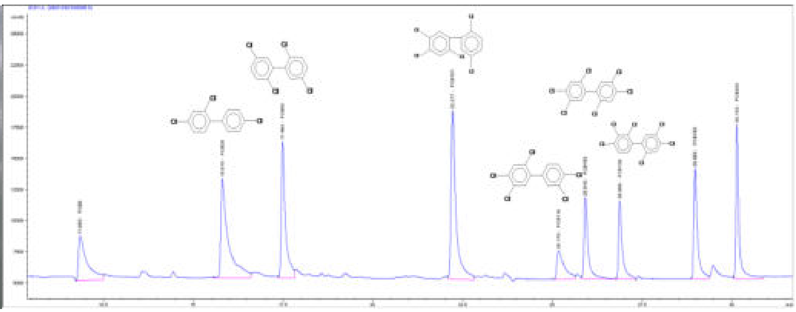

Fig. 2. GC ECD chromatogram of the six indicator PCB congeners.

Biodegradation Assay using Biostimulation/Bioaugmentation Approaches
Biodegradation was carried out in Erlenmeyer flasks equipped with sorbent Silipor (0.5 g) column that was closed with a cotton wool stopper to maintain sterile environment and allow gas diffusion. This apparatus for simultaneous monitoring of evaporation and biodegradation of PCBs was described previously [20]. The apparatus allows determine mass balance of the tested compound. The evaporation rate constants of the individual PCB congeners presented in Delor 103 were published in our previous papers [21]. To assess aerobic biodegradation of PCBs present in long-term contaminated sediments from Strážsky canal with autochthonous microflora under biostimulation conditions, 0.75 g of cut plant material containing terpenes (ivy leaves or pine needles) was added to 50 g of wet sediment. Biodegradation was carried out under stationary conditions with intermittent mixing at 28 °C in the dark. The control for the abiotic decrease of PCBs was represented by sterilized sediment. The samples were analyzed at the beginning of the experiment and on the 7th, 14th, and 21st days. Total flask contents were taken for PCB analysis. To evaluate aerobic biodegradation of PCBs in the bioaugmented sediments, 50 g of dry sediment and inoculum of *Pseudomonas stutzeri* with the final concentration 1 g.l^{-1} in the minimal liquid media mixed with the sediment and replaced into the apparatus were used. The cultivation conditions were the same as in an experiment with non-bioaugmented sediment.

Soxhlet Extraction
A sample of the sediment was desiccated at laboratory temperature and sieved using 71 µm diameter sieves. Two g sediment and 0.5 cm layer of Na_2SO_4 were added into the Soxhlet apparatus. The sediment was covered with cotton wool moisturized in chloroform. A 100 ml extraction flask with 40 ml of n-hexane as extraction medium was attached to the apparatus. After 1 hour, 20 ml of n-hexane was added and the extraction was continued for 3 hours. The column was washed by n-hexane. The cleaning procedure was repeated to obtain transparent extract. Subsequently, after concentration at vacuum evaporator, 1 ml of n-hexane was added and content was transported to the test tube. The prepared sample was analyzed using GC. The extract was concentrated on vacuum evaporator to the final volume 1 - 2 ml, 1 g of copper powder was added to eliminate sulphur and the mixture was ultrasonicated for 45 min. Subsequently, the mixture was filtered through 5 cm of florisil layer.

PCB Extraction and GC ECD Analysis
The sediments were extracted for 4 h in the Soxhlet apparatus with n-hexane, filtered and purified through a 5 cm layer of florisil until the sample became transparent. One µL of the n-hexane extract was injected into the Hewlett-Packard gas chromatograph HP7890A. Separation of the PCBs was performed on a capillary non-polar column HP-5 (30 m × 0.32 mm inner diameter) coated with 0.25 µm (5%-phenyl)-methylpolysiloxane phase. Electron-capture detector (300 °C) was utilized, helium was used as carrier gas (flow rate 1.8 ml.min^{-1}), and nitrogen as make-up gas (25 ml.min^{-1}), the pressure was 68.13 kPa. The temperature program was as follows: the initial temperature 80 °C for 1 min, followed by an increase at a rate of 30 °C.min^{-1} until the temperature reached 160 °C and then kept at the temperature 1 min, followed by an increase at a rate of 4 °C.min^{-1} until the temperature reached 260 °C and then kept at the temperature 3 min. The total time of analyses was 32.7 min. The

indicator PCB congeners recommended by EPA were analyzed (Fig. 2). Calibration solution was prepared for PCBs 8, 28, 52, 101, 118, 138, 153, 180, and 203. Quantitative evaluation of the results was performed based on comparison of the peak areas corresponding to the indicator congeners in the chromatograms of the samples and of the standards.

RESULTS AND DISCUSSION

The presence of active autochthonous adapted microflora in the sampled long-term PCB-contaminated sediments was confirmed in our previous work. Our results revealed that with the more contaminated sediment of Strážsky canal higher biodegradation was determined than in less contaminated sediment of Zemplínska Šírava water reservoir, both located in PCB-contaminated area [19]. Currently, we have isolated using 16S rRNA phylogenic analysis of 15 bacterial strains with PCB degradative ability from the studied historically contaminated sediments. Five from them revealed PCB degradative ability [18]. Aerobic and anaerobic biodegradation of PCBs in the contaminated sediments occurred and is continuing, but very slow during the least invasive bioremediation approach natural attenuation. Biodegradation can be accelerated by nutrient or inducer addition during the process of biostimulation, and/or by inoculum addition (autochthonous or allochthonous), using a bioaugmentation strategy to promote the degradation of target contaminant, PCBs. Successful bioaugmentation is dependent on the following criteria: (1) the microorganisms must be able to survive and compete with indigenous microorganisms, adapt to the natural environment, and resist toxins in hazardous waste sites, (2) microorganisms must be able to preserve their degradative ability, i.e., express appropriate enzymes capable of degrading target compounds, and (3) the microorganisms must have contact with the contaminant for degradation reactions to take place. Then, in our work PCB degrader with detected bph gene was used, and bioavailability of the individual PCB congeners in the contaminated sediments was determined. In addition, suitable growth conditions and appropriate nutrient supplements are essentials for added microorganisms to adapt to the environment [22].

Our attention was in this work focused on biodegradation of PCBs in the natural sediments using biostimulation and/or bioaugmentation approaches of bioremediation. Biodegradation experiments were performed a) in the intact (untreated) sediments by autochthonous microbial consortium under biostimulation conditions with addition of plant terpenes as inducers [23, 24], b) in the bioaugmented sediments inoculated by the above mentioned bacterial isolate from long-term PCB-contaminated soil *Pseudomonas stutzeri* [17], and in combination of both used approaches, biostimulation and bioaugmentation. The *bphA1* gene, encoding enzyme biphenyldioxygenase responsible for PCB degradation, was identified in a genome of the bacteria *P. stutzeri* in our previous work [19]. Presence of this important enzyme makes these bacteria attractive and prospective candidates for application as bacterial degraders suitable for the bioaugmentation of PCB-contaminated biotopes.

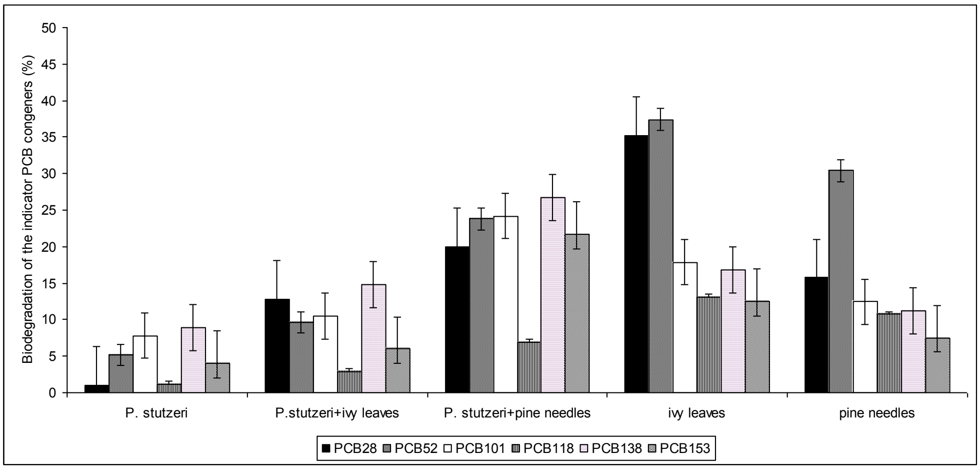

Fig. 3. Biodegradation of the indicator PCB congeneners under bioaugmenation, biostimulation, and combination of bioaugmentation and biostimulation conditions in the PCB-contaminated sediments in the presence of *Pseudomonas stutzeri* inoculum and plant terpenes as the potential inducers (ivy leaves and pine needles, addition of 0.75 g cut plants). Cultivation conditions: 20 g of dry sediment with 100 ml of minimal mineral media, pH 6.5, initial concentration of inoculum $1 g.l^{-1}$, 28 °C, in the dark, 21-day stationary cultivation with intermittent mixing.

Number of CFUs of the indigenous soil microorganisms present in sediment sampled from Strážsky canal was about 5×10^5 in 1 g of the dried sediment used in bioaugmentation strategy) and about 7×10^6 in 1 g of the wet sediment (used in biostimulation strategy). The results obtained during biostimulation with pine needles were comparable with those obtained under the conditions of biostimulation combined with bioaugmentation (addition of *P. stutzeri* and ivy leaves) (Fig. 3).

When the indigenous microbial population is present in the contaminated area, the addition of exogenous inoculum reveals very often not the expected synergistic but antagonistic effects due to competition of microorganisms towards substrate. The results indicate slightly antagonistic rather than synergistic effect of indigenous and exogenous bacteria. Under bioaugmentation conditions, degradative bacteria *P. stutzeri* was added as a biocatalyst to the sediment to strengthen biodegradative ability of indigenous microorganisms. The relationship between biodegradation, bioaccumulation of PCBs in fish, and bioavailability will be discussed in the lecture. The results revealed that higher biodegradation of the indicator PCB congeners occurred under biostimulation than under combined bioaugmentation and biostimulation conditions. According to the results, biostimulation seems to be an efficient method to enhance biodegradation of PCBs using natural capacity of the long-term adapted indigenous microbial consortium. The method may allow solving the problems with survival and colonization ability of the inoculated degraders.

We assume that our findings might be of high relevance for development of sediment-specific remediation technologies. Information obtained from microcosm studies performed with naturally contaminated sediment, plant inducers, and autochthonous inoculum might be also useful in the preliminary design of a site-specific biostimulation/biaugmentation strategy. In this area, much new knowledge is needed, in terms of commercially available nutrients, electron donors/acceptors, suitable bacterial degraders, individual strain or microbial consortium, and the technologies enabling their efficient incorporation into the contaminated sediments. In spite of still existing gaps, it is possible to say that bioremediation represents a potential ecological and economical alternative to decontamination of areas polluted with low concentrations of chlorinated aromatic pollutants.

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BROFISCIN QUARRY REMEDIATION SCHEME, CARDIFF, WALES.

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KEYWORDS

Contaminated land, significant contaminant linkage, groundwater, surface water, human health, risk assessment, PCBs, VOCs, monitoring, remediation.

ABSTRACT

Once described as the ‘most polluted place in the UK’, Brofiscin quarry lies on Carboniferous limestone, a Principal Aquifer and Site of Special Scientific Interest. It was landfilled with ~72,000m^3 industrial wastes from 1965 including drummed liquids, VOCs, SVOCs and PCBs. The quarry did not benefit from a liner, leachate/vapour management system or engineered cap. Residential properties were built directly to the south up bedrock dip.

The UK Contaminated Land Regulations adopted in Wales (2001) incorporate inspection strategies, risk assessment and remediation. Investigations were completed to develop the Conceptual Site Model (CSM) and identify pollutant linkages. In March 2005 the quarry was determined as contaminated land under Part IIA of the Environmental Protection Act 1990. Environment Agency Wales became the regulator to secure remediation and recover costs from original polluters.

Following data interpretation a remediation scheme incorporating a cap with HDPE membrane and pressure relief system was designed. The primary objective of the scheme was to limit recharge and prevent direct contact with waste. The scheme commenced in 2011 and was successfully completed in 2012. Long term monitoring of groundwater, surface water, ambient and bedrock vapour concentrations continues. This paper discusses the scheme in detail and revisions to the CSM.

BACKGROUND

Brofiscin Quarry is situated to the north west of Cardiff and north of Groesfaen in Rhondda Cynon Taf County Borough, South Wales at National Grid Reference 306899 181246. The site is bounded in the south west, south and south east by residential dwellings and farmland elsewhere. The quarry site covers an area of 1.49 ha and when limestone extraction ceased, the resulting void was used for the disposal of industrial wastes, including drummed liquid waste from 1965 to 1970 under planning consent by the local authority. Waste disposal legislation did not exist at the time the quarry was infilled. The consent included the following condition.

“That the waste shall be deposited in the western part of the quarry to a height not exceeding the level of the main quarry floor.” (the height of quarry floor not defined).[1]

Fig. 1. Aerial Photographs courtesy of Welsh Government [(21/07/1967; 24/01/1971 and recent (NRW)]

The waste deposited at the quarry has been filled to a level which is some 13m below the crest of the original quarry high-wall. The in-filled waste level within the quarry reaches a nominal 70m above Ordnance Datum. Residential development in close proximity to the quarry was granted planning consent on 11th September 1987 by the local authority. The properties do not benefit from enhanced protection measures and used standard strip footings.

ENVIRONMENTAL LEGISLATION RELEVANT TO BROFISCIN

The Town and Country Planning Act 1947 provided a comprehensive code for planning control. This Act has been added to several times and consolidated in 1990. It provided a mandatory national framework for development control with many basic functions that have remained constant. Section 57(1) identifies that planning permission is required for any permitted development, which includes mining, land reclamation and building operations.

In 1972, as a result of 36 drums of sodium cyanide ash being illegally dumped near Bermuda village, Nuneaton, England on 24th February 1972 the Deposit of Poisonous Waste Act 1972 (DoPWA) was implemented to regulate waste disposal. The Control of Pollution Act 1974 superceded the DoPWA improving regulation of waste disposal and pollution issues. Noise, atmospheric pollution, trade and sewage effluent discharges to relevant waters were prescriptively described.

On 24th March 1986 a landfill gas explosion occurred at a residential property constructed close to a municipal landfill site at Loscoe, Nottinghamshire. Three occupants escaped serious injury and the incident led to new environmental controls, through Government circulars. Article 18 of the General Development Order 1988 required that the Planning Authority consult the Waste Regulation Authority (WRA) for any development within 250m of land used for the disposal of waste within the last 30 years.

The WRA could seek that suitable conditions be attached to a consent or object to an application. Circular 1/85 required that conditions should not be attached unless justified on clear grounds.[2] Typical conditions require an assessment of land quality to ensure relevant precautions can be agreed and adopted to minimise risk prior to the condition being formally discharged.

The Environmental Protection Act 1990 (EPA) was introduced in the UK and within Part III, Section 79 required local authorities to check its area from time to time for nuisances. Landfill gas and contamination from previous activity could be considered under the nuisance provisions.

When The Environment Act 1995 was implemented, Section 57 inserted Part IIA and Section 78 (contaminated land) into the EPA. The provisions of the EPA were implemented by subsequent secondary legislation. The Contaminated Land (Wales) Regulations 2001 came into force on 01st July 2001 and were accompanied by statutory guidance from government. The legislation adopted the polluter pays philosophy. The UK government made funds available for the assessment of contaminated land in England and Wales in 2000.

Local authorities are required to prepare inspection strategies and to inspect their areas from time to time to identify contaminated land. The statutory guidance requires this to be undertaken considering contaminant-pathway-receptor linkages (often referred to as pollutant or contaminant linkages) and risk assessment. The nuisance provisions under Part III of the EPA relating to contaminated land were repealed.

GEOLOGICAL SETTING

The site lies on the southern limb of a large regional syncline that plunges to the west. The sequence of Old Red Sandstone, Carboniferous limestone and the Upper Carboniferous Coal Measures were folded with south to north compression during the Hercynian orogeny. The Coal Measures of the South Wales coalfield outcrop at the centre of the syncline with limestone outcropping on the northern and southern limbs.

The Quartz Conglomerate Group as the upper formation of the Old Red Sandstone outcrops 300m to the south. NNW to SSE faulting across the syncline has formed large fault controlled blocks. This block is some 3Km long and lies between the Miskin fault to the west and the Creigiau fault to the east, both downthrown to the west. Two similar trending faults up to 150m to the south west of the landfill have displacements of 90m and 15-18m.[3]

Heamatite mineralisation in the upper sequence was exploited at Llanharry 6Km to the west. Galena at the base of the limestone is referenced by Barber[3] as locally exploited within the block 400m to the south west. This may have been as a trial as it is not referenced in the geological memoirs.[4 & 5]

SOLID & DRIFT GEOLOGY

The Carboniferous sequence is up to 565m thick[3] and the strata at the quarry and underlying the surrounding houses are the Dinantian (Lower Carboniferous) Black Rock Limestone Group. This includes the Barry Harbour Limestone, Brofiscin Oolite and Friars Point Limestone Formations that strike 270° broadly east west and dip 27° to 35° north. Vertical jointing is evident along two strike directions 20° and 345°. The Cwmynyscoy Mudstone is immediately to the south, which is part of the Lower Limestone Shale Group.

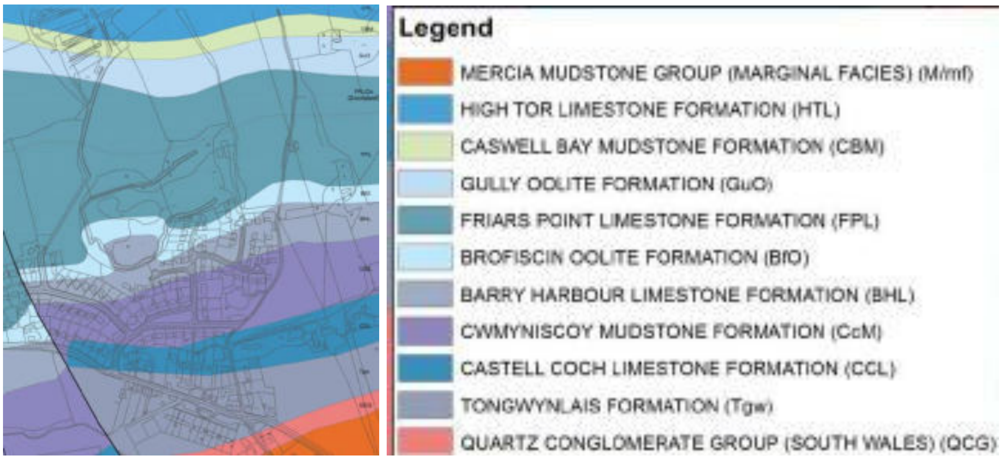

Fig. 2. Geological Setting [URS[6]]

The five fracture sets identified[7] include:
i] Bedding plane fractures, average dip 30° north with spacing governed by bed thickness (0.14-1.97 m);
ii] Vertical fractures perpendicular to the bedding planes and trending north-south, average spacing 0.89 m;
iii] Fractures at an average strike and dip of 142° and 71° (dominant dip direction not established);
iv] Fractures perpendicular to the bedding planes and trending east-west with a dip of 60° south;
v] Fractures at an average strike and dip of 28-45° and 65° (dominant dip direction not established), average spacing 2.36 m.

The site is designated as a Site of Special Scientific Interest (SSSI) as it is the only location in the region where the Brofiscin Oolite is exposed. The section through the Black Rock Group displays deeper marine environments sandwiching the oolite as a southerly advancing shoal typical of a marine sand bank.

A tongue of Devensian glacial till is identified to the east of the site that extends laterally wider northwards towards the Mwyndy Brook. Elsewhere in the immediate vicinity outside of the extent of the quarry, superficial soils of varying thickness cover the limestone bedrock with infrequent rock outcrop observed.

HYDROGEOLOGY

The location is on a topographic high and radial groundwater flow is feasible, however with northerly dipping strata, preferential groundwater flow in a northerly direction is dominant.

Carboniferous limestone is a fissured Principal Aquifer sometimes used within Wales as a local or major potable source. Groundwater levels in Carboniferous limestone can fluctuate by up to 20m. Seasonal affects of between 7.3 and 9.7m were recorded at Brofiscin for Department of Environment (DoE) boreholes BB1 to BB3.[8] Carboniferous limestone typically has a low primary porosity and negligible intergranular flow,[3] with secondary porosity from fractures, bedding and solution features being key to groundwater movement. Permeability and transmissivity from fissure flow can be large especially if cavities or conduits are present.

Groundwater emerges locally as several springs to the east, south and south west. The junction between the Quartz Conglomerate Group and Carboniferous limestones to the south provide a natural spring line.[9] A spring line to the north is present where the superficial clay rich glacial till terminates on the Carboniferous limestone by Brofiscin Fach, near Mwyndy Brook.[8]

Near to Brofiscin all properties are on mains water with only minor abstractions previously used for isolated or older farming property, ie Maendy Farm over 400m to the north west and Llwyn-y-pennau 550m to the south west.[3] The nearest abstraction is on the west of the block or on golf courses to the north of Mwyndy Brook.

Old mineral workings along strike have standing water and at Llanharry continuous dewatering of the heamatite workings was required as inflows occurred via faults, fissures, cracks and vugs (small irregular cavities) in the limestone.[3] During quarrying at Brofiscin groundwater was intercepted at a low level in the southern face and collected to form a pool 6 to 7.5m deep in the south of the quarry[2].

HYDROLOGY

Annual average rainfall at Cardiff is reported as 1100mm and at Cardiff Airport 950mm. Groesfaen is further inland and Barber[3] used a value of 1500mm and an effective rainfall of 980mm. A weather station installed in 2011 at the site recorded 1727mm rainfall for 2012, the second wettest year on record.

At Brofiscin surface water collected within the quarry and slowly drained from the waste to the north east into a ditch that drains onto farmland where in periods of high rainfall surface water collected.[3] A drain along the field boundary was reported to connect the pond to the Mwyndy Brook at Brofiscin Fach where the topography naturally sheds rainfall. [3] Mwyndy Brook flows west into the River Clun and then southwards into the River Ely and the Severn Estuary. Minor tributaries on the Carboniferous limestone can be ephemeral and the drainage ditch at Brofiscin was observed to be mostly dry[3] in the summer months.

DEPARTMENT OF ENVIRONMENT STUDIES

In 1978 the Department of the Environment published research into hazardous waste at varied UK landfill sites often referred to as the *"Brown Book"*.[1] Brofiscin Quarry, like the nearby Maendy Quarry, was identified as receiving only industrial and trade wastes both as solids and liquids. Wastes were deposited between 1965 and early 1970 and included wastes from Monsanto Co Ltd, BP Chemicals Ltd, ICI (British Nylon Spinners) Ltd and Pyrene Ltd.[3] All companies assisted in a preparing a detailed inventory of waste deposited at Brofiscin and its' sister site Maendy. The estimated disposal rate of 6,100 tonnes/year covered both sites.

Tab. 1. Waste Materials deposited at Maendy & Brofiscin reported to the Welsh Office[3]

Source Material	%
Petroleum additives (Ba based)*	43.3
Petroleum additives (Ca based)*	4.9
Petroleum additives (Zn based)*	1.4
Pentachlorophenol*	0.4
Silicon esters*	1.2
Sanctocure*	2.1
Arochlors*$	2.2
Maleic/phthalic anhydride$	0.4
4-Nitrodiphenylamine$	16.8
Santoflex$	1.2
Plastics	18.2
Office, stores, research etc	7.9

* Filter cake $ Distillation residues

This included approximately 130T over five years of distillation residues and filter cakes containing solid PCBs (sometimes corresponding to Arochlors 1254 and 1260) and terphenyls. Other wastes included petrochemical wastes, various solvents, hydrocarbons and metal bearing wastes. Building, wood and office wastes and plastics were deposited with the chemical waste, but no domestic waste. Other recorded key trace compounds included phosphorous pentasulphide, alkylbenzene sulphonates, aluminium salts, p-nitrochlorobenzene, formanilide, 4-nitrodiphenylamine, aniline, phenol, styrene-butadiene, naphthalene, tars and vanadium salts. [3]

A monitoring programme of leachate and spring waters commenced in late 1973, though peak strength of surface leachate was reported by the Welsh Water Authority, presumably from infrequent spot samples, from late 1970 to mid 1971. The report concluded that heavy rainfall flushed organic substances from the landfill, though during periods of low flow contaminant quality was improved. [3]

Herbage and soil samples from the ditch and adjacent field in April 1974 identified appreciable accumulated iron and zinc concentrations. Total Organic Carbon (TOC) concentrations were recorded as low in adjacent springs and surface waters (<4 - 11mg/l) and in surface leachate as 20 – 190mg/l. [3]

Three rotary air flush boreholes were installed up to 100m depth between November 1976 and February 1977. Boreholes BB2 and BB3 were installed with difficulty due to unstable conditions from clay and marl bands plus a reported loss of air circulation in cavities. In borehole BB1, 30m to the north and drilled to 76m with 300mm of soil cover, offensive odours were detected at 65.5m forcing the crew to wear respirators. Similar odours were identified at 28.5m in BB1, at 21m and below 66m in BB2. Groundwater on one occasion from BB1 samples at depths greater than 60m, measured 450 -1,070mg/l TOC. [3]

The borehole construction details and monitoring protocols are not recorded. Fleet[8] implies that the boreholes were constructed as open hole allowing vertical interference when sampling and subsequent surface water recharge became more likely.

Erratic or spasmodic results from BB1were however revealed. In March 1977 only background concentrations of TOC, chloride, phenol and metals were recorded. By July 1977 higher than background levels of TOC and phenol were recorded and in November 1977 equivalent concentrations to those recorded during drilling were identified. This intermittent appearance of substances was thought to indicate leachate movement in pulses at various levels in the landfill.[3] This was reaffirmed from monthly monitoring conducted between 1977 and 1980[8] which identified seasonal variation in groundwater quality, with concentrations peaking during November and low concentrations occurring in March for 1977 and 1978. After 1979 results became stable.

The report displayed the quarry as having a "U" shaped profile and its five conclusions[3] were
i] The leachate had a high organic load;
ii] Surface water recharge built up to overflow to surface ponds in the north east of the landfill;
iii] PCBs and metals present in low concentrations in leachate are retained by solids such as sediments in the drainage channels and areas of overflow;
iv] Deeper leachates are more concentrated than near surface leachate, with intermittent slow diffuse movement of leachate from different levels of the landfill; and
v] The extent of pollution is unquantified, but a high degree of vertical leachate movement indicated. No pollution of springs was identified.

ENVIRONMENTAL ASSESSMENT REPORTS (2000-2004)

Environment Agency Wales (EAW) screened potential sites in Wales and progressed the assessment of land at Brofiscin Quarry in 2000. Substances previously deposited at the site were considered to have the ability to potentially form significant pollutant linkages (SPLs) either as significant pollution of controlled waters or as significant possibility of significant harm (SPoSH).

Initial work comprised a desk study, followed by a water features survey,[9] a vapour survey[10] and environmental assessment.[11] Soil and herbage analysis indicated that VOCs and PCBs were present in the quarry with up to 17mg/kg VOCs and 21.56mg/kg PCBs with one recorded VOC off site and traces of PCBs. Surface water sampling identified values on site up to 2.16mg/l Σtarget VOCs and 5.6mg/l Σtarget SVOCs, whereas only very low levels were recorded offsite.

Soil vapour monitoring used driven 1m stainless steel spikes in the unsaturated zone, both within the quarry and around the residential area. Monitoring after purging three times revealed a list of VOCs on site, but at only one location off site, VOC traces were recorded from a total of 33 locations. No groundwater investigation was undertaken and the assessment identified a range of uncertainties (temporal) with respect to transport and impacts of substances to controlled waters, residents and site users. The interpretation of groundwater levels from spring lines and use of previous reports developed the CSM further.

A subsequent assessment[12] installed five boreholes (BHs1-5) in waste that were drilled to rockhead at depths up to 6m below ground level (bgl). Combining intrusive surveys with ground conductivity, electro-magnetic and resistivity tomography geophysical surveys identified that chemical waste was limited to the west. Typically 3m of demolition waste was found in the east. Spike and flux box monitoring confirmed the chemical waste was not producing significant methane quantities, hence diffuse vapour flow, not pressure driven flow is prevalent.

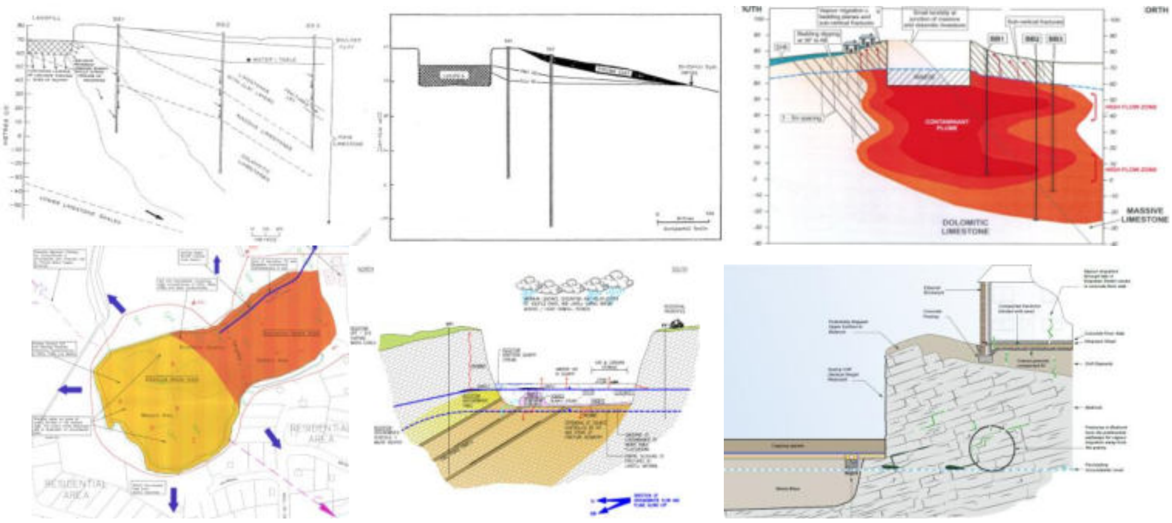

Fig. 3. Conceptual Site Model Cartoon Development 1978,[3] 1983,[8] 2001,[11] 2003[12], 2007,[13] 2013[6]

DETERMINATION AS CONTAMINATED LAND & FURTHER ACTIONS (2005 – 2007)

The local authority determined the site as "contaminated land" in March 2005. Sixty-seven significant controlled water pollutant linkages (SPLs) were identified. The site was formally designated as a Special Site under regulation 3c (i) and (ii) and EAW as lead regulator continued a series of investigations.

Following designation, a preliminary remedial options appraisal was undertaken by EAW[14] and a number of Remedial Assessment Actions (RAAs) in advance of any Monitoring Actions and/or Remedial Treatment Actions (RTAs) were identified. These actions include further site investigation and monitoring to further develop the CSM so that a clear conclusion can be reached on which RTAs represent the best practicable technique. Other groups of potential pollutant linkages (PPLs) clearly exist; however the local authority was unable to establish their significance from the information and guidance available.

Tab. 2. Significant Pollutant Linkage Groups summarised from the Record of Determination[15]

Contaminant Groups	Pathway	Receptor
VOCs, SVOCs, PCBs and Metals contained within the waste	Leaching & mobilisation of contaminants by downward percolation of rainwater & fluctuating groundwater levels	Groundwater in the limestone aquifer
VOCs, SVOCs, PCBs and Metals contained within the waste	Groundwater flow & surface water run-off from the quarry	Surface water features within the quarry
VOCs, SVOCs	Volatilisation & mobilisation of contaminants & subsequent partitioning between the gaseous and aqueous phase	Surface water features within the quarry and groundwater

Six groundwater boreholes/multi level monitoring wells were installed up to 70m bgl in and around the quarry[16] to determine the lateral and vertical extent of groundwater contamination. This was followed by twelve months of surface water and groundwater sampling and development of a new CSM.[13]

REMEDIAL OPTIONS APPRAISAL (2008)

A further Remedial Options Appraisal[17] identified a preferred remedial package of a combination of surface water treatment of water in the ditch and monitored natural attenuation (MNA) of groundwater. The selection reflected the practical difficulty and cost benefits of treating deep groundwater pollution, but also the potential pollution impacts to surface waters. It identified a number RAAs in order to implement the remedial package.

A subsequent water balance survey[18] identified that on site leachate boreholes (BHs 3&4) had a direct correlation with rainfall. Flow in the ditch to the north of the quarry exhibited a time-lagged calculated effective rainfall. Combined this indicated that the waste possesses a storage capacity and when rainfall was sufficient following drier periods that leachate levels rose from a baseline and overtopped into the ditch for approximately half the year. Discharges ranged from 0 to 500m^3/d , with few points above 300m^3/d. Leachate levels were perceived to drain quickly and limited groundwater outflow from the quarry (to the ditch) occurred. It was considered that further examination of options to surface water treatment may identify alternative solutions.

As the drainage ditch was dry for approximately half the year the opportunity to use a treatment process with reed beds was compromised. The Cost Benefit Analysis for MNA[19] identified firstly degradation of substances to daughter products and the presence of indicator substances (DO, nitrate, sulphate, alkalinity) confirm that degradation in the subsurface was favourable for a wide range of substances. Secondly that the only recognised readily financial saving is not having to undertake water treatment for future potential groundwater users. This was primarily due to the lack of groundwater use (no monetisable benefit) and no impact to down gradient receptors. Improvements for both would register no monetary benefit. A RAA to install additional down gradient boreholes was discounted by Welsh Government as the benefit of demonstrating an improving groundwater quality had a low increased confidence. The preferred RAA included aquifer management looking to confirm no further deterioration of groundwater quality and absence of contamination at discharge locations in receiving waters via a monitoring programme.

At this point the local authority commissioned its own investigation at the site looking to establish if significant harm is being caused or there is a SPoSH being caused to human health from waste deposited at the quarry.[20]

THE REMEDIATION DESIGN (2010)

An outline design for an engineered cap using the CSM was requested, which combined with aquifer management was considered to resolve more issues in a cost effective manner than trying to augment water supplies to ensure treatment could effectively operate. It also addressed human health PPLs identified by the local authority investigation. The capping scheme[21] was designed to prevent leachate recharge through infiltration and limit onward pollution of controlled waters. The reduced recharge would limit leachate generation and thus outflow towards the ditch, which would only occur during periods of higher rainfall. Effluent quality would be enhanced by the dilution effects of collected rainfall discharged as clean surface water into the ditch. The water quality and loading could be monitored post cap completion in order to assess whether further treatment was required. The design also prevented direct physical contact with chemical waste.

The cap comprised a soil regulating layer, under membrane pressure relief drainage for vapours, a welded 2mm HDPE synthetic cap, an over membrane surface water collection drainage system and restoration soils. The synthetic cap had a perimeter anchor trench within the waste, excavated to just beneath the lower summertime (baseline) leachate level, which is intended to act as a lateral barrier limiting vapour diffusively migrate offsite. A thickened fillet of soil was laid at the quarry edge to promote drainage inwards and the HDPE liner here was double rough sided. The vapour collection pipework was set out as two ring mains, an inner and an outer, connected to vent points that could be monitored to establish venting arrangements and if post works monitoring determined a vapour treatment system should be retrofitted.

With funding confirmed by the Welsh Government in May 2011 the project team were able to commence liaison with Rhondda Cynon Taf County Borough Council with regard to securing planning consent. A key step to aid this process is to demonstrate a community consultation has been undertaken and the application has accommodated community concerns where possible.

To aid this process all residents were invited to an open informal surgery held at the local chapel on 15th June 2010. The hand delivered invitation letters included generic details of the remediation scheme and timing of twelve weeks timescale. The design engineer, key project staff and local authority environmental health officers attended using design drawings, example products and residents asked many questions especially about the timing and frequency of the expected 1000 lorry movements or ~25 lorries/day if moving five days a week over nine weeks. Whilst the consensus of residents was favourable for remediation to progress, key concern was the traffic movement through residential roads and onto a narrow single track country lane, plus vibration when lorries accessed the quarry track.

A number of residents had expressed that lorry movements were limited outside of the “school run” ie after 9:15 and before 15:30hrs. In order to control traffic movements and pedestrians a Traffic Management Plan[22] was prepared using radio, traffic lights and stop go methods. The vegetation along the B class road was cut back to create better visibility and to comply with Section 59(3)(a) of the Highways Act 1980 a nominal sum was paid to the Highways Authority to mitigate potential negative traffic impacts. The Traffic Management Plan was formally submitted with the lorry timelines requested by residents and agreed with the local authority. This had a financial impact on the project as lorries were hired on a daily basis and soil movement efficiencies were lost.

Residents adjacent to the quarry access track and narrow “B Class” road were contacted and arrangements made to undertake both pre and post remediation work “defect” or “stock condition” surveys of properties by an independent Chartered Surveyor. Within the tender for the works, a requirement to resurface the quarry access track was included to prevent lorries causing vibration by bouncing in the potholes. These elements were incorporated in the Environmental Monitoring Plan[23] (EMP) as were monitoring of the environment for nuisance and environmental performance. Vapours and controlled waters were key to this. The controlled waters and hydro-ecology were being monitored as part of the ongoing Long Term Monitoring Plan (LTMP), that had already had over a dozen monitoring rounds undertaken as part of the aquifer management programme.

Vapours in ambient air and bedrock from boreholes were also scheduled to allow two monitoring rounds prior to work commencing. Using six shallow peripheral boreholes (BH2–BH7)[20] drilled from 4.20 to 6.60m bgl in the surrounding residential development, a strategy to use both long term down hole vapour sampling at hourly intervals using photo ionisation detectors (PID) and also by extracting vapours after purging three well volumes through a sample train via the same sorbent pumped diffusion tubes as utilised by the earlier human health study.[20] It wasn’t clear if the initial data had been collected following purging, however as this was best practice it was included in the EMP.

The GasClam PID had not been used previously at the site and measured VOC’s (LoD 1ppm), temperature, barometric and differential pressure and bulk gases CH_4 and CO_2. Monitoring using initially two instruments and later a third commenced on 24th August. The borehole diffusion tubes were using twin bed sorbent (Tenax/Unicarb) diffusion tubes with a factory supplied pump. Passive air quality diffusion tubes used chromasorb sorbent. Analysis was undertaken by the same laboratory as per the previous study. The following management plans were also appended to the formal planning application 11/0831/10 of July 2011 to help ensure conditions attached to the consent became simpler and not requiring documents to be formally submitted and agreed. A Surface Water Management Plan[24] to accommodate surface water discharges and the dismantling and re-construction of an up gradient draining culvert, constructed by the owner in the lower section of the ditch. The planning consent was passed at a special committee on the 01st September 2010.

A Materials Management Plan[25] was prepared which stipulated the geotechnical and chemical quality of the soils to be imported for use within the regulating layer and restoration soils. The scheme was intended to be flexible to allow a lower specification of non waste soil materials to be used if the contractor was comfortable with the source, however the Plan identified the type, frequency of monitoring and analysis required for each source as validation and subsequent verification on receipt at site. A range of chemical quality for total and leachable parameters were selected, the latter becoming a hindrance due to the time taken for leachability analysis. Tonmawr quarry overburden was sampled in late September and began being imported on 18th October. In hindsight it would have been more effective to have adopted a shorter suite of total substances.

Ecological surveys were also undertaken to establish reptile and mammalian activity at the site. Foraging bats were occasionally detected and grass snakes were identified at the site. The length of time taken to conduct a number of the surveys and then implement mitigation measures such as snake capture and safe release meant that vegetation clearance at site could not be conducted until after this was completed (12th -15th September).

A Pilot Environmental Management Plan[26] was submitted and outlined the construction activities and management procedures available to mitigate nuisance, impacts to the environment and the SSSI. The document outlined the alert levels used that would trigger review, monitoring and/or further action.

The contractor mobilised to site on 13th October which broadly coincided with a deterioration in weather, Persistent rain fell during the formation layer being proof rolled, deployment of the regulatory layer and the under liner drainage layer. Imported soils had demonstrated a mean shear strength of 46kPa and a capacity to achieve a shear strength greater than 50kPa. By the end of October, even after soil surfaces had been sealed, it was evident that the soil brought on to act as the regulatory layer was becoming incapable of sustaining heavy plant traffic. A redesign was necessary and the Contractor proposed either to withdraw until the spring or using Verdatex 60/60, a woven geotextile, placed on materials already deployed with 40-100mm quarry won stone placed on top to provide a working platform for the excavators. An opportunity existed to trial a Type 1 material that comprised up to 10% tarmac road planings instead of the virgin quarry won stone, however the Type 1 material contained a greater portion of fines and when trialling it was self evident that it would not have supported excavators with either the short or long reach arms when fully loaded. By issuing a specification for a coarser recycled aggregate this may have been possible, but time to implement and a higher cost for recycled product ensured that quarry stone was the only viable option.

During trialling of the woven geotextile and quarry won stone, the contractors foreman reported that when driving his machine on the south of the site and also on the north east, the ground was much firmer than and not as springy as in the middle of the site. It was thought that a "U" shape quarry was unlikely and quarry benches probable, especially to get access to lower working levels. Additional aerial photographs were provided by the Welsh Government after construction had started, which also implied the existence of quarry benches. The theory of rock benches was put to the test with a series of trial pits from the quarry perimeter leading into the quarry on the southern edge and then later in the north east. PPE with breathing masks and portable PID instruments calibrated for benzene, toluene and VOCs were used.

Fig. 4. Cap Design, Rock Benches & Pressure Relief System[Geotechnology[27]]

The results confirmed a rock bench gently dipping north for approximately 25m at its widest. The bench has a mantle of primarily quarry wastes with a thin veneer of black ash tapering from nothing at the quarry perimeter to up to ~30-45cm at the rock bench. No chemical waste was noted in the black ash. The rock bench was revealed abruptly and displayed a blocky face on the side wall. Alarms on instruments sounded frequently when the trenches excavated wastes within the confines of rock benches, often revealing chemical wastes and occasionally drums. This stimulated further vapour monitoring and all personnel working within the quarry during periods of excavations or when welding were required to use face fitted breathing masks.

Subsequent investigation revealed an equivalent rock bench of some 10m in the north east, though a tongue of waste some 2m wide was noted to protrude into this area, both rock benches were surveyed in. This also caused a redesign as the CSM with a "U" shaped quarry was proven incorrect. The benched quarry profile actually provides a longer pathway in strata between residents to the south and chemical wastes. Using similar design principles the line of the perimeter trench was changed where rock benches were present. The geocomposite pozidrain 7S250D/NW8 used on site for liner protection, vapour drainage and as a surface water drainage medium, was used as liner protector on the irregular rock face. The pozidrain also acted as a means to allow residual vapour between the liner and the irregular rock face to be collected and transmitted to a relief vapour collection pipe on the rock bench where it diffusively dissipated at two vent points.

The use of pozidrain to act like a drainage ring main around the site caused a redesign at the east of the quarry. When moving out of the chemical waste at the neck of the quarry into inert quarry waste materials, the design engineer did not want leachate to rapidly transmit at a depth of up to ~1.5m towards the headwall where the relief leachate drainage could over top into the drainage ditch at the north of the quarry. Accordingly once the perimeter trench in the north and south left the chemical waste within the confines of rock benches, the use of pozidrain was stopped and the design allowed for the HDPE liner to be set in a bentonite clay for ~4m length. To the east of these bentonite plugs the HDPE liner acted as an anchor trench directly laid against inert waste/quarry overburden.

Construction works re-commenced on 18th November and rapidly provided a firm sub-base on which to install relief vapour drainage and lay the geocomposite layers and HDPE liner on the southern rock bench. Excavations for the perimeter trench commenced near the start of the southern rock bench and progressed in an anticlockwise manner. Excavations occasionally revealed chemical waste contained in 45g drums, however this became frequent and often as the contractor progressed north along the west quarry wall and then east along the north quarry wall. Drums were often reasonably intact, with free product occasionally observed. Odour was managed by covering waste and returning all arisings to inside of the perimeter trench following construction or reburying in a quarantine area at the edge of the trench. Monitoring with portable PIDs was continuous. Due to construction starting later than initially anticipated, the prolonged inclement weather caused operational delays and redesign issues. The project remained flexible to continue until the end of January 2012 to bring in, lay and seal the restoration soils, pending installing minor surface water field drains and dressing the site in the spring.

The winter weather caused erosion of surface soil within the quarry and washed away fines, leaving a stony surface. 2012 was the second wettest in a century and minor works were not completed until September 2012 and included importation of 2,000T topsoil for the quarry prior to hydroseeding the site.

MONITORING RESULTS

The LTMP focussing on controlled waters commenced[28] in 2010 a particularly dry year (983mm) but includes all monitoring from 2006. The LTMP adopted alert levels such as a borehole becoming blocked, increasing pollutants in boreholes or water quality standards (WQS) failures on three occasions and macro-invertebrate score deteriorate downstream. Of the six monitoring wells installed, the four wells selected for aquifer management include MW1 (up gradient), MW6 (cross gradient) with MW3 and MW5 (down gradient). Presently an allowance to conduct the LTMP for up to ten years has been made, should monitoring dictate. The first year comprised six monitoring visits and to date there have been 23. Although there have been difficulties at times with purging multi level ports, samples have been taken when well head parameters stabilise or the following day when the well has recovered after being pumped dry. The results confirmed that MW3 suffered the greatest impact with benzene, TPH, GRO, vinyl chloride, 1,2 DCA, total PCBs and nine other organic substances in excess of 100 or 1000 times their respective alert levels. Additional substances were present at MW3 and TPH, acenaphthene and fluorene (10-100 x alert level) plus chloroform, TCE and PCE (1-10 x alert level) were measured in some ports in MW1, MW5 and MW6. From current monitoring (2011-2012) MW3 continues to show gross hydrocarbon pollution at depth, however MW6 and MW5 show low levels of pollution which may be directly related to heavier rainfall witnessed supporting the groundwater CSM.

When assessing surface waters during the same period, the surface water within the ditch has exhibited an equivalent range of substances, although analysis of surface water in the field (when present) or downstream at Brofiscin Fach or in the Mwyndy Brook show only very low levels of five organic substances and one occasion when PAH and pentachlorophenol were above their WQS, indicating that widespread or continuous surface water pollution was not occurring. Since remediation work commenced, water quality monitoring has identified infrequent marginal exceedances of 1,2 DCA WQS in Mwyndy Brook.

Tab. 3. Results of Biological Monitoring 2009-2012

Site	Location	BMWP 20/08/2009	Taxa N° 20/08/2009	ASPT 20/08/2009	BMWP 30/11/2012	Taxa N° 30/11/2012	ASPT 30/11/2012	ASPT Mean
1	250m u/s	66	14	4.7	88	14	6.3	5.4
2	25m u/s	48	10	4.8	61	11	5.5	5.1
3	55m d/s	70	14	5	95	17	5.6	5.8
4	310m d/s	87	17	5.1	86	16	5.4	5.3
5	900m d/s	-	-	-	95	16	5.9	5.8

Biological studies have been conducted every six months over the last four years (seven events) on the Mwyndy Brook to the north of Brofiscin quarry, where the overtopping leachate has historically discharged when draining from the ditch over the farmers' field. The results of one minute macro-invertebrate kick sample results do not show deterioration of quality. The Biological Monitoring Working Party scores provide an indication of quality and the average score per taxa indicates the population structure and if pollution is impacting. The Higher BMWP scores downstream indicate that the discharge from the quarry is not impacting the Brook and up to three high scoring pollution sensitive taxa are found in downstream samples. The LTMP continues.

The GasClam instruments were removed from Boreholes in August 2012 after twelve months. Since boreholes were purged, no elevated results were identified in any of the boreholes, except once when the instrument was malfunctioning and recording elevated results in air and with calibration gases. The instrument was returned for servicing. The inference was that even though the pumped diffusion tubes were recording trace levels of VOCs, the values for the GasClams were at or below the level of detection (1ppm).

Diffusion tube results confirm a heterogeneous mix of trace organic substances, that vary both spatially and over time. This perhaps reflects the distribution in the waste mass, substance mobility, the proximity of the waste to relevant fracture sets and the length of pollutant pathways. The trend has identified that since initial work during 2008 to 2010, the concentrations for BHs 3-7 have shown a general reduction in total vapour concentrations within the bedrock surrounding the quarry, although fluctuation in the vapour concentrations and the composition of those vapours persists. An example is provided in Figure 5.

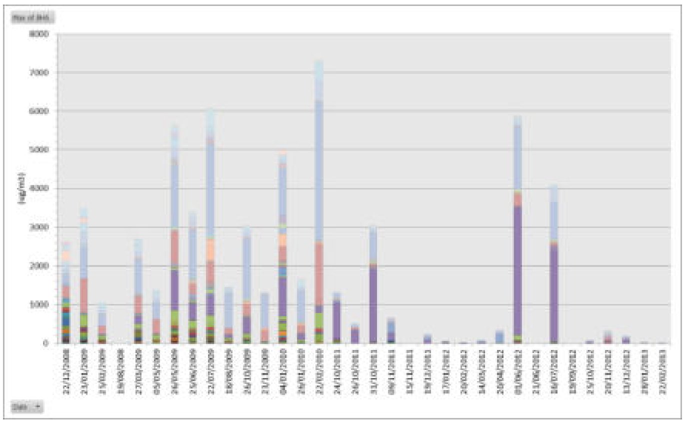

Fig. 5. Temporal variability and composition of vapours detected in BH6

In total, over 350 different chemical substances have been identified in the bedrock vapour samples; dominated by aliphatic and aromatic petroleum hydrocarbons. It is not known what the initial vapour concentrations and compositions that developed in the bedrock subsequent to the disposal of the waste in the quarry were, or how those concentrations and compositions have varied in the intervening forty years. The vapour concentrations detected in the bedrock are significantly lower than those detected in boreholes installed in, and flux boxes installed above, the waste mass which have been recorded at up to 610 mg/m^3. Vapour release from the quarry is expected to be greatly limited by the very high groundwater level in the waste.

Ambient air monitoring within and around the quarry shows very little change over the monitoring period. Total VOC concentrations are shown in Figure 6, and indicate marginal differences between the quarry and its immediate surroundings. Over seventy different chemical substances have been identified in the ambient air samples; again dominated by aliphatic and aromatic hydrocarbons. Where standards exist for individual substances, the detected concentrations are within UK and EU air quality standards.

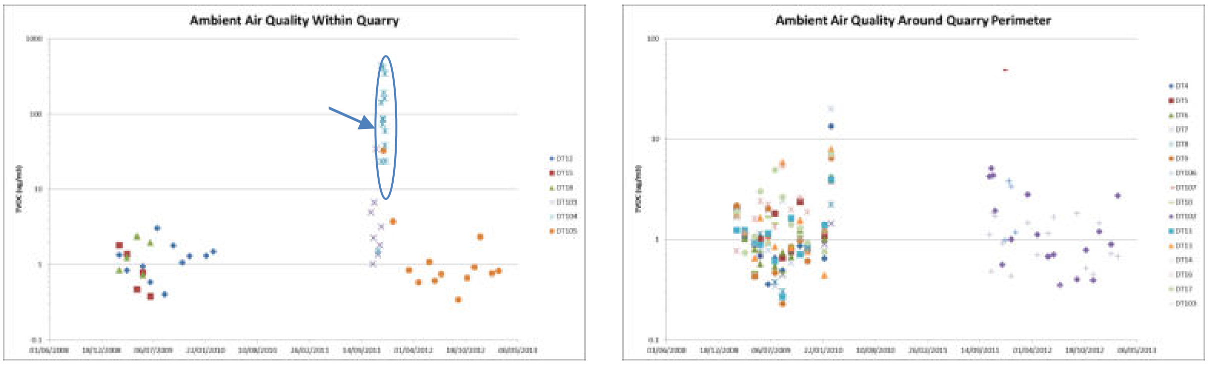

Fig. 6. BH7 Temporal variation & BH2 Concentration Variation 2008-2013

CONCLUSIONS

A separate superficial deposit study[29] using a dynamic probe to contour the soil bedrock interface in residential areas was undertaken. This was used within a review of the vapour CSM[5] and if adopting current data sets and the statutory guidance,[30] the vapour impact to human health of adjacent residents can be considered to be sufficiently small to meet the category 4 site definition. That is "land that has been excluded from the need for further inspection and assessment because contaminant levels do not exceed relevant generic criteria.......". Only categories 1 and 2 meet the statutory definition of "contaminated land". The LTMP continues to assess impacts to controlled waters as part of the aquifer management strategy.

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MAJOR MILESTONES AND ACCOMPLISHMENTS OF REMEDIATION AT LOGISTICS SITES IN SLOVNAFT, a. s.

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KEYWORDS

Contaminated sites, soil and groundwater remediation, oil pollution, Slovnaft Logistics, environmental burdens at Slovnaft Logistics sites, Benzinol

ABSTRACT

Existence of the Slovak refinery Slovnaft is historically connected with its distribution partner company, called Benzinol. Benzinol developed a net of terminals providing wholesale services for commercial clients and storage of petroleum product reserves for the state. Beginnings of its operation stretch back to early 50's of the 20th century. At that time the first Logistics terminals had been constructed - some of them built at formerly operated areas, used as distribution centers. Development of the logistics network continued during more than 30 year period, over which the Environmental protection standards significantly changed.
Soil and groundwater contamination occurred at many areas, mostly caused by technologic incidents, low awareness of the personal or poor technologic equipment. The first attempts for clean-up can be traced to middle 70's. These activities were usually based on pump&treat technology in combination with soil excavation. More complex methods were applied from the end of 80's. After acquisition of Slovnaft by the MOL Group company it was decided to launch an integrated program for remediation at Logistics terminals. This decision was made at the time of missing clear legislative regulation for contaminated sites. Slovnaft applied risk-based management at the contaminated sites as one of the first in the Slovak Republic. Twelve sites were involved in the project, which comprised ecological audits, geological surveys and risk assessment. Remediation had started at 9 of them. At present the contamination is eliminated to acceptable limits at 6 sites. The process was in all main steps consistent with actual legislative requirements.

OVERVIEW

Storage and handling with petroleum products at Logistics terminals lead to groundwater and soil contamination several decades ago. Sometimes it happened without generally visible signs and could stay unnoticed, as many product pipelines and storage tanks were situated underground. Extent of contamination was consequently revealed by execution of geological surveys. Pollution was often found in surroundings of manipulation and re-filling technologies: rail tank-car loading station, road tank-car loading station, pumping stations, unloading technologies, refilling stations or storage tank farms. Each terminal developed a set of boreholes for groundwater quality monitoring or, in necessary cases, started groundwater pumping and clean-up. These activities were partially successful.

Logistic terminals typically stored several types of petroleum products - gasoline, diesel, aviation gasoline, lubricant oils, heating oil or used oil. Even though the contaminant source was mostly known, the geological survey in the first phase included a wide range of analyzed contaminants. Their presence, however, was not proven.

In case of revealed water pollution, the governing legislative - the Water Act - required execution of recovery measures. The site clean–up started after obtaining necessary permits from the local state authorities.

PROJECT MILESTONES

The systematic approach for remediation projects was taken in Y 2002, named SAGAL (Soil And Groundwater Assessment of Logistics sites). The target remediation values for total petroleum hydrocarbons (TPH) were set for each site according to the risk assessment studies. As the size of the project required planning in phases, the internal process in the first place involved rough categorization and prioritization, which was performed by an expert company. The sites scores were calculated from points assigned for different environmental aspects as well for a status of the technologies. Consequently, the risks to human health and environment were evaluated. The used methodology was almost identical with the currently valid directive of the Slovak Ministry of Environment. It was proven that risks to human health were not present or, in case of hypothetical short term activities, could be easily eliminated by use of the personal protective equipment. On the other hand the significant ecologic risks were found arising from high mobility of contaminants that could pose a threat for wider areas.

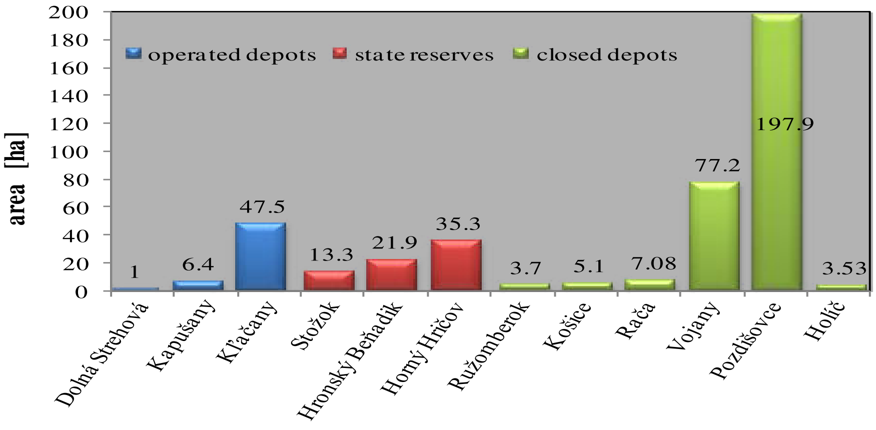


Fig. 1. Slovnaft logistics terminals by the type and size of area

The whole process was divided into phases:

Project SAGAL
1. Environmental screening and review from archive sources
2. Scoring and prioritization
3. Risk analyses elaboration, setting target remediation limits and preliminary implementation study
4. Detail geological survey (if the uncertainties of the risk assessment were high)

Project SIMPLE (Sagal IMPLEmentation)
5. Remediation project elaboration
6. Remediation works
7. Update of the Risk assessment
8. Post monitoring
9. Removal of the boreholes and technologies, change to operational monitoring if requested

The remediation started at the sites with highest risk scores – Pozdišovce and Ružomberok, as the first in Y 2004, followed by Hronský Beňadik, Stožok, Horný Hričov, Bratislava-Rača and Košice in Y 2006. Remediation at Holíč depot started as the last one, in Y 2010. The remaining 3 sites were continuously monitored.

METHODS AND ACHIEVMENTS

During the initial phase of remediation it was revealed that chlorinated solvents and polyaromatic hydrocarbons, originally identified by the risk analyses, were not present in the groundwater in concentrations exceeding limits. TPH analyses detected in IR spectrum were used as a representative parameter for remediation control. The primary advantage of the applied analytical method was the convenient price for analyses and overall comparability within the sites as well as with historical records. TPH measurements were combined with the use of BTEX or PAH analyses, which provided good control of the contamination extent and remediation progress. Other parameters like nutrients content, microbiology, pH and redox potential were analyzed according to the project specification, to ensure control of discharged water quality and condition for natural attenuation in the saturated and unsaturated zone.

The applied principle of management of contaminated sites required removal of free petroleum product from the ground water table, at all locations where found, and clean-up of groundwater and soil to the target limits. The work started by revision of the technologies, their cleaning and demolition of those identified as a contamination source (underground tanks, pumping station, refilling stations, etc.). At some terminals it was followed by soil excavation. The contaminated soil was treated on place utilizing existing impervious surfaces, adapted for soil decontamination according to the state authority requirements.
The soil excavation was not applicable everywhere. Sometimes it was limited by an existence of the operated technologies or was extremely expensive. At such cases the in-situ remediation methods were applied.

Groundwater remediation was the most time demanding process. For groundwater pumping and infiltration, boreholes or drainages were used with respect to the local geologic conditions. The treatment methods were chosen according to the type of contamination representing a mixture of diesel, gasoline and oil in different ratios and degradation rate. Typically there were built more separate treatment units at each site. Thus their size and type could be optimized according to the characteristics of the local hot-spot. Groundwater quality discharged from the treatment units was controlled on monthly base and used for re-infiltration. Controlled infiltration helped to increase the flushing rate of contaminants from the both saturated and unsaturated zone. Removal of the adsorbed contamination was increased by addition of detergents (NPAL), showing good efficiency to release remains of contaminants non removable by water. Applications were done in separate campaigns, evaluating results after each. The subsequent effect was improving conditions for biodegradation processes. The efficient radius for application of additives or solvents can be rather small, so it usually required to build a dense set of application boreholes. Air sparging and vapor extraction were also applied at contaminated zones with significant part of volatile content. If desired results could not be achieved within a given time schedule, chemical oxidation was used for a clean-up in the final phase. Before its application we had to overcome a fact that the method had not yet been implemented in Slovakia and some of the local authorities wanted to restrict the use of chemical oxidation. To eliminate any uncertainties, the general use of the reagents was applied only after a small scale pilot test, accepted by the approving authority.

Fig. 2. Removal of the underground storage tanks at Bratislava-Rača

Remediation was controlled by a supervising company. Supervision included on-site audits, parallel sampling, analyses in the independent laboratory, approving results, measurements, validating reports and optimizing financial efficiency of the works.

Management of the remediation projects required:

In the preparation phase:

- Preparing project data, project outline, defining goals and requirements according to legislative
- Manager approvals and support
- Promote cost analyses and decision (conduct remediation or use more passive measures to protect a site and encourage natural attenuation)
- Approval of the implementation project
- Arrangement of financing

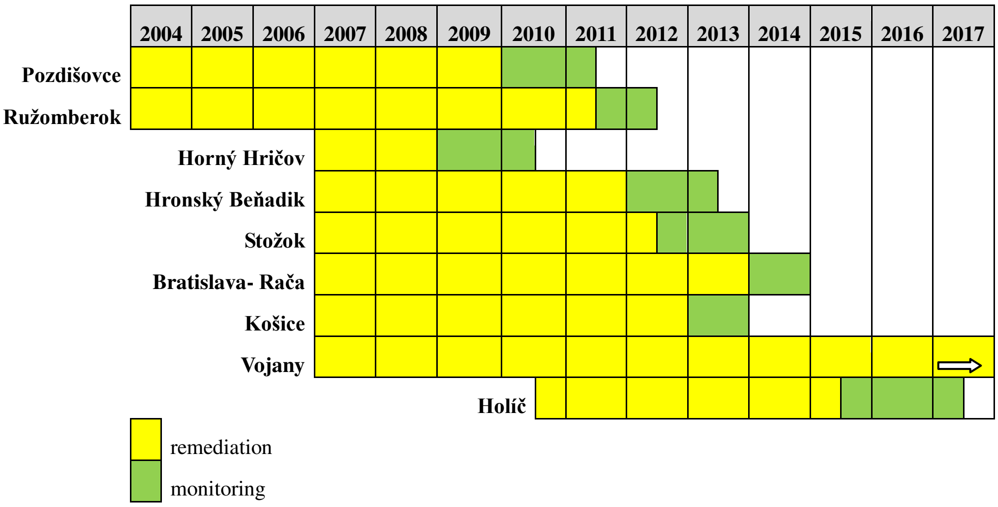
In the implementation phase

- Participation in tender and contracting of expert companies
- Follow-up of the timeschedule and milestones
- Review and validation of reports
- Budget control
- Preparing reports
- Review of technical content

Continuously

- Communication with all involved parties
- Follow-up of the conditions set by the state authorities

Remediation works were finished when monitored contaminants achieved the target limits in more than 95 percent. Impact of residual concentration was evaluated during risk assessment update. The benefit of repeating this procedure was that measurements and results collected during remediation works were used to eliminate the earlier uncertainties. Post remediation monitoring was the final part of works, typically executed in 2 rounds within 1 – 2 year period.



	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
Pozdišovce	🟨	🟨	🟨	🟨	🟨	🟨	🟩	🟩						
Ružomberok	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨🟩	🟩					
Horný Hričov				🟨	🟨	🟩	🟩							
Hronský Beňadik				🟨	🟨	🟨	🟨	🟨	🟩	🟩				
Stožok				🟨	🟨	🟨	🟨	🟨	🟨🟩	🟩				
Bratislava- Rača				🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟩			
Košice				🟨	🟨	🟨	🟨	🟨	🟨	🟩				
Vojany				🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨 ⇨
Holíč							🟨	🟨	🟨	🟨	🟨	🟨🟩	🟩	🟩

🟨 remediation

🟩 monitoring

Fig. 3. Remediated terminals in timescale

The scope of the SIMPLE project was remarkable: up to 80 underground tanks were removed from the Logistics stores, above 4,5 mil. cubic meters of groundwater was treated during remediation, over 120 thousand tons of contaminated soil was biodegradated to the target limits at decontamination plots, number of built boreholes counts in hundreds, as well as length of drainages in meters. Slovnaft invested 11,1 mil. € for remediation works performed in the SIMPLE project.

CONCLUSION

Contaminated sites clean-up can be a significant obstacle for industrial companies to overcome. Besides the enormous costs for remediation, the project management can be particularly difficult given that it requires knowledge of specific legislative standards and directives. It differs from the typical business oriented projects following standard internal processes. First of all, there exists a high degree of uncertainty associated with subsurface remedial works. Changes in the project are very common, and should be expected. Some financial reserve can help to overcome difficulties in resolving such situations. Changes of the environmental legislation can also impact remedial approaches and associated costs. This particularly was a problem in the past decade. It should be noticed, however, that implementation of the new legislation has started only very recently and standard procedures are just being set. The whole process is strictly followed up by the state authorities and requiring their separate approvals. According to the specific lows the local offices can impose further conditions to the works.

Slovnaft, as environmentally responsible company, had started remediation at its sites long before a relevant legislation was in place and belonged among a few exceptions in Slovakia in the past two decades. Performed works brought valuable experience for the Slovak environment in application of techniques and development of methodic approaches in groundwater and soil remediation.
After many years of attempts the remediation at Slovnaft Logistics depots reached noticeable results. Contamination was eliminated to acceptable level at six out of nine remediated sites. Remediation at other three depots is in progress.

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ENVIRONMENTAL EXPOSURE TO ENDOCRINE DISRUPTORS AND SELECTED METABOLIC MARKERS IN CHILDREN

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KEYWORDS
Environmental contamination, endocrine disruption, obesity, polychlorinated biphenyls, adipokines, children

ABSTRACT

Obesity is a major global health problem. Adipokines are metabolically active proteins, produced by fat cells (adipocytes), affecting metabolically active tissues and regulating several neuroendocrine axes. There is raising concern about the influence of chemical exposure on obesity and the role of environmental exposure to endocrine disruptors in the alteration of metabolism. A first set of candid ate obesogens was proposed, among others including persistent organic pollutants (POPs).

Region of Michalovce in Eastern Slovakia was contaminated by PCBs as the result of former PCB production in the area. Cohort of children, born and living in the Michalovce region, was followed from birth up to 7 years of age.

First results on the association between PCB exposure and levels of selected adipokines in children will be presented and discussed, within the context of hypothesis on Developmental Origins of Health and Diseases (DOHAD hypothesis).

INTRODUCTION

The prevalence of obesity gradually increases worldwide in both, developed and developing countries. Obesity is a chronic disorder that has multiple causes, including genetic, behavioural and environmental factors. Increasing evidence points to the early life experience being the important risk factor in obesity development using birth weight as a proxy measure for the quality of intrauterine life. It is well established that there is a relationship between impaired early growth and the subsequent development of adult disease ("developmental origins of health and diseases"; DOHaD hypothesis) (Armitage et al., 2008).

Adipose tissue is not just a passive lipid repository, but an active secretory organ sending out and responding to signals, Adipocytes secrete metabolically active proteins known as adipokines, the major ones being leptin and adiponectin (Fantuzzi, 2005). Leptin´s primary biological function is the regulation of food intake and energy expenditure at the hypothalamic level. Adiponectin is a key molecule in "metabolic syndrome", it has a regulatory effect on insulin sensitivity and it affects hepatic glucose production.

There is raising concern about the influence of chemical exposure on obesity and the role of "environmental obesogens" (Grun and Blumberg, 2009a). Obesogens can be defined functionally as chemical agents with endocrine disrupting properties that inappropriately regulate and promote lipid accumulation and adipogenesis to favour weight gain and obesity (Grun and Blumberg, 2007).

Persistent organic pollutants (POPs) are toxic lipophilic compounds, highly resistant to degradation. They bioaccumulate and biomagnify in the food chain and are widely distributed in the environment. The main source of exposure to human population represents fatty food of animal origin. Because these compounds contaminate virtually all people, even if they present only a low individual risk of diabetes and obesity, they might have a substantial overall population effect (Porta, 2006). Typical representatives of POPs are selected organochlorine compounds, e.g. polychlorinated biphenyls (PCBs), organochlorine pesticides incl. DDE, dioxins and furans. PCBs are toxic endocrine disrupting chemicals, with negative effects on immune, nervous and reproductive systems. They belong to developmental toxicants.

Region of Michalovce in Eastern Slovakia was contaminated by PCBs as the result of former PCB production in the area (within 1959-1984). As the result of the PCB production with the subsequent contamination of the surroundings due to the improper waste management, PCB levels in blood in the Michalovce population are among the highest in the world. Our results showed that although the human PCB exposure is slowly decreasing, the risk of deleterious health effects on human population is still present (Trnovec et al., 2010).

The main aim of the presentation was to asses the effect of prenatal and postnatal exposure to polychlorinated biphenyls on the levels of selected adipokines (leptin and adiponectin) in 7-year-old children living in Michalovce region.

METHODS

Cohort of children, born and living in the Michalovce region, was followed from birth up to 7 years of age. At the age of 7 years, levels of leptin and adiponectin were measured in venous blood samples (N=270) using ELISA method. Selected PCB congeners in cord blood and at the age of 6 years were analyzed by high-resolution – gas chromatography (HR-GC). Information on health status and socio-demographic and environmental characteristics was collected in cooperation with regional pediatricians and using questionnaires. Data were statistically analyzed using STATA 6.0 for Windows. Multiple linear regression was used for assessment of the association between prenatal and current PCB exposures and the levels of adipokines.

RESULTS

Data on PCB exposure of children in our cohort was published already (Sonneborn et al., 2008; Trnovec et al., 2010). Actual weight of a child represented a strong predictor for leptin ($r=0.64$, $p<0.001$), but not for adiponectin levels. Higher levels of leptin were found in Caucasian children, compared to Roma children, in girls and in children of mothers who did not smoke in pregnancy. Regression model adjusted for ethnicity and gender showed negative association of leptin levels with current PCB exposure (Table 1), but no association with the prenatal PCB exposure. Adiponectin levels were inversely associated with cord blood PCBs but this relationship disappeared after adjustment for other variables.

Tab. 1. Regression model for the association between the levels of leptin and PCB exposure at the age of 6 years in children

	Parameter estimate	**SE**	**p value**
Log (PCB153 6Y)	-0.44	0.096	< 0.001
Gender (0, 1)	0.39	0.206	0.059
Etnicity (0, 1)	-0.64	0.306	0.039

DISCUSSION AND CONCLUSIONS

Obesity is not simply a product of overeating and lack of exercise; instead, the accumulation of fat or mobilization of lipids from adipose storage depots is controlled by a variety of factors (Grun and Blumberg, 2009b). Exposure to obesogens may result in the mis-regulation of critical pathways involved in adipogenesis, lipid metabolism, or energy balance. PCBs were suggested to effect adipocyte differentiation and production of proinflammatory adipokines (Arsenescu et al., 2008) and energy and lipid homeostasis (Kim et al., 2011). Our preliminary findings support the hypothesis that exposures to endocrine disruptors in infancy and childhood interfere with metabolic pathways, although we did not find the effect of prenatal PCB exposure, but postnatal – current PCB exposure was found to be associated with the levels of leptin in 7-year old children.

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POSTER SECTION

INTERNATIONAL CONFERENCE
CONTAMINATED SITES BRATISLAVA 2013

BRATISLAVA May 29 –31, 2013

Nr.	Presenter/ Name Surname	Poster Title
1	**Hana Dudášová (SK)**	BIOAUGMENTATION STRATEGY USING FIVE BACTERIAL STRAINS ISOLATED FROM PCB-CONTAMINATED SEDIMENTS
2	**Lucia Lukáčová (SK)**	BOTTOM SEDIMENTS CONTAMINATED WITH POLYCHLORINATED BIPHENYLS (PCBs) AND THEIR ECOTOXIC AND MUTAGENIC EFFECT
3	**Slavomíra Murínová (SK)**	THE ADAPTATION RESPONSES OF CYTOPLASMIC MEMBRANE ON THE ENVIRONMENTAL STRESS MEDIATED WITH POLYCHLORINATED BIPHENYLS (PCBs) AND 3-CHLOROBENZOIC ACID (3-CBA)
4	**Radovan Karkalic (SRB)**	NEW TECHNOLOGICAL APPROACH FOR THE PERSONAL MICROCLIMATE COOLING PROCESS IN THE HIGH TOXIC CONTAMINATED SITES
5	**Leonid Perelomov (RUS)**	LANTHANUM ADSORPTION BY AL-PILLARED CLAY IN THE PRESENCE OF ORGANIC ACIDS WITH DIFFERENT FUNCTIONAL GROUPS
6	**Irina Perelomova (RUS)**	ADSORPTION AND OXIDATION OF AS SPECIES IN MODEL BIO-MINERAL SYSTEMS
7	**Bozena Smreczak (PL)**	AVAILABILITY OF PAHS IN SOILS – FACTOR CONTROLLING BIOREMEDIATION EFFICIENCY
8	**Barbara Maliszewska-Kordybach (PL)**	INTERPRETATION OF CONTAMINATED SITE DEFINITION – – HOT SPOTS AT AGRICULTURAL AREAS
9	**Agata Godlewska-Hejduk**	THE CHEMICAL ASPECTS OF THE IN-SITU CHEMICAL OXIDATION (ISCO) OF SOILS FROM CHOSEN ORGANIC COMPOUNDS (PAHs, CHCs)
10	**Martin Murín (SK)**	CONTAMINANTS – "TRADITIONAL" AND REACH LIMIT VALUES – SUBSTITUTION OR CONTROVERSY?
11	**Najiba Afandiyeva (AZ)**	REMOVING OF THE PESTICIDE REMNANTS

12	**Luke Beesley (UK)**	THE ROLE OF BIOCHAR IN THE PHYTOREMEDIATION OF METAL/METALLOID CONTAMINATED SOILS
13	**Tamara Roznerita (MD)**	REMEDIATION OF POPs POLLUTED SITES IN MOLDOVA
14	**Giuseppe Buccheri (I)**	APPLICATION OF RISK ASSESSMENT PROCEDURE TO A REFINERY LOCATED IN A COASTAL SITE WITH NATIONAL INTEREST (ITALY)
15	**Ion Barbarasa (MD)**	INTEGRATING, SOCIAL, TECHNOLOGICAL AND ECONOMIC ASPECTS IN ENVIRONMENTALLY SOUND MANAGEMENT OF POPS DISPOSAL-LESSONS LEARNED FROM MOLDOVA
16	**Jamsran Tsogbaatar (MGL)/ Katarína Paluchová (SK)**	ESTABLISH THE GEO-DATABASE ON ECOLOGICAL HEALTH OF THE MILITARY SITES IN MONGOLIA
17	**Simona Žajdlíková (SK)**	APPLICATION OF THE INTEGRATED REMEDIATION SYSTEM DURING REMEDIATION OF GROUNDWATER AND ROCK ENVIRONMENT POLLUTED BY OIL PRODUCTS
18	**Katarína Bučinová (SK)**	THE ACCUMULATION OF MACRONUTRIENTS BY MACROFUNGAL SPOROCARPS FREQUENT FROM VICINITY AN ALUMINIUM SMELTER
19	**Renato Baciocchi (I)**	EVALUATION OF BIODEGRADATION DURING THE VAPOR INTRUSION OF PETROLEUM HYDROCARBONS
20	**Marcela Blahutová**	THE IMPORTANCE OF THE INVOLVEMENT OF STAKEHOLDERS IN STEERING COMMITTEES OF THE NATIONAL CONTAMINATED SITES INVENTORY PROJECT (NIKM)
21	**Wawan Budianta**	REMEDIATION OF CONTAMINATED SOIL BY NATURAL ZEOLITE
22	**Ekaterine Imerlishvili, Alverdi Chankseliani**	CONTAMINATED SOILS IN GEORGIA
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24	**Vojtech Vilinovič, Andrea Hurtíková, Martin Zatlakovič**	GROUNDWATER HYDRAULIC PROTECTION (GWHP) SYSTEM OF SLOVNAFT REFINERY

BIOAUGMENTATION STRATEGY USING FIVE BACTERIAL STRAINS ISOLATED FROM PCB-CONTAMINATED SEDIMENTS

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KEYWORDS

Bacterial strains, bioaugmentation, biodegradation, contaminated sediments, PCBs

INTRODUCTION

Polychlorinated biphenyls (PCBs) are hazardous, persistent environmental contaminants strongly bound to soil [1] and, because of their relative volatility and high chemical stability, they have been largely dispersed and detected in all compartments of the ecosystem, including air, water, soil, sediments, and living organisms in the past and at present. PCBs are highly lipophilic and their bioaccumulation along the food chain makes even low environmental concentrations a threat for the wildlife and human health [2]. Nowadays it is very important to minimize pollution caused by PCBs. Several bacterial species with the ability to degrade PCBs have been isolated from contaminated soils, sludges and aquatic environments, and they have been studied extensively [3]. Bioremediation is really suited to be applied for decreasing the usually high energy demand and consumption of chemical reagents in vast and moderately contaminated soils [4]. One of the ways to enhance the efficacy of contaminant removal is bioaugmentation [5, 6]. This strategy is based on the inoculation of given soils with microorganisms, pure or mixed cultures, characterized by desired catalytic capabilities [7].

The aim of this study was to identify microorganisms isolated from PCB-contaminated sediment sampled from Strážsky canal, to examine their capability to degrade PCBs in liquid medium as well as in PCB-contaminated sediment and to establish whether they possess the *bphA* gene encoding 2,3-biphenyldioxygenase, the first and the most important enzyme of the degradative pathway responsible for the bacterial ability to degrade PCBs.

MATERIAL AND METHODS

Bioaugmentation strategy for isolated bacterial strains

Dry PCB-contaminated sediment, 20 g, was placed in 250 ml Erlenmeyer flasks with 100 ml of liquid MM medium. Each bacterial strain was cultivated for 48 h in the growth medium No. 2 at 28 °C and after centrifugation at 3200 rpm for 20 min, the biomass was diluted in distilled water and taking calibration into account, the concentration was measured as absorbance at λ=620 nm. Each bacterial strain was added to the dry sediment and liquid MM medium in the final concentration of 1 g/l. The control was prepared with sediment and liquid MM medium. All samples were cultivated in three parallels at 28 °C for 21 days and at simulated natural conditions.

After 21 days of bioaugmentation, the sediment was centrifuged at 4000 rpm for 20 min and then left to dry on air. The dried sediment was analyzed by Soxhlet extraction and GC (Agilent 7890A) in cooperation with the Water Research Institute in Bratislava, Slovakia.

Soxhlet extraction

The amount of 2 g of dried sediment sieved through 2 µm pores were placed into a Soxhlet extractor (Sigma-Aldrich, Germany). Extraction using 60 ml of *n*-hexane lasted 4 h. After 4 h, a teaspoon of powdered copper was added and the sample was placed into an ultrasonic bath for 45 min. Filtration was done to get the copper out of the sample through a florisil column. *n*-Hexane was vaporized. Each sample was placed into an eppendorf and diluted with n-hexane to the volume of 1 ml. The samples were analyzed by GC (Agilent 7890A). The effectiveness was considered as well.

GC-ECD analyses of PCBs

Samples were analyzed on an Agilent 7890A GC with He as the carrier gas (68.13 kPa, 1.8 ml/min, split) and N_2 as the „make up“ gas (25 ml/min, the whole volume flow of 64.8 ml/min, septum flow of 3 ml/min and „purge“ flow to „split“ in 2 min (60 ml/min) with an Agilent 19091 J-413 column (30 m × 320 µm × 0,25 µm). Temperature program: initial temperature of 80 °C - 30 °C/min – 160 °C - 4 °C/min (1 min) – 260 °C (3 min) (Agilent Technologies, USA). Identification of peaks and their calibration was performed using a standard mixture of six indicator PCB congeners (PCBs 28, 52, 101, 118, 138, and 153).

RESULTS AND DISCUSSION

The aim of this study was to identify 15 isolated bacterial strains using the 16S rRNA gene sequencing PCR-based method and consequent sequencing. The BLAST sequences comparison provided the following results: *Microbacterium oleivorans* (EU867300), *Stenotrophomonas maltophilia* (HM047520, HQ185399), *Brevibacterium* sp. (EU333894), *Ochrobactrum anthropi* (EU187487), *Pseudomonas mandelii* (FN811901), *Rhodococcus* sp. (GU324716), *Achromobacter xylosoxidans* (HQ426648), *Stenotrophomonas* sp. (GU202014), *Achromobacter* sp. (HM217265), *Ochrobactrum* sp. (HQ652577), *Pseudomonas aeruginosa* (FJ841974) and *Starkeya novella* (CP002026).

The *bphA* gene was detected only in the *A. xylosoxidans* (H8) strain by both preliminary and PCR based detection method. The other strains produced multi-band profiles through the *bph* PCR assay.

Bioaugmentation of PCB-contaminated sediment using the selected five bacterial strains showed very promising effect on the indicator PCB congeners present in the sediment. The best degradation of indicator PCB congeners present in the sediment was monitored for *Achromobacter* sp. *Achromobacter* sp. removed PCB 28 (36%) and 52 (35%) the best from the contaminated sediment while degrading also PCB 101 (28%), PCB 118 (6%), PCB 138 (5%), and PCB 153 (8%). *S. novella* and *A. xylosoxidans* had similar degrading effect on all six indicator PCB congeners except for PCB 153. Degrading ability of *S. novella* on indicator PCB congeners was as follows: PCB 28 (29%), PCB 52 (20%), PCB 101 (15%), PCB 118 (3%), PCB 138 (9%), and PCB 153 (9%). *A. xylosoxidans* with detected *bphA* gene showed degrading ability on indicator PCB congeners as follows: PCB 28 (27%), PCB 52 (16%), PCB 101 (9%), PCB 118 (5%), PCB 138 (7%), and PCB 153 (1%). The degrading ability of *O. anthropi* (13%) and *P. mandelii* (15%) was the highest from all five bacterial strains for PCB 118.

CONCLUSION

Achromobacter sp. degraded tri- and tetrachlorinated biphenyls the most of all five used bacterial strains. *S. novella* and *A. xylosoxidans* had similar degrading effect on all six indicator PCB congeners except for PCB 153. In the presence of *P. mandelii* and *O. anthropi* the highest biodegradation of the pentachlorobiphenyl PCB 118 was observed.

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BOTTOM SEDIMENTS CONTAMINATED WITH POLYCHLORINATED BIPHENYLS (PCBs) AND THEIR ECOTOXIC AND MUTAGENIC EFFECT

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KEYWORDS
Ames test, Delor 103, genotoxicity, *Lemna minor,* PCBs, *Vibrio fischeri*

INTRODUCTION

PCBs are classified as the most persistent and toxic industrial compounds that have been detected as contaminants in almost every component of the global ecosystem. They represent serious ecological problem due to their low degradability, high toxicity, and strong bioaccumulation. For living organisms, they represent potential health risks as a consequence of their lipophilic nature, toxicity, and possible carcinogenic properties [1]. It has been recognized that PCBs elicit rather chronic than acute effects in humans [2]. Most PCBs in the environment are bound in soil and water sediments close to the places of their former production and application [3]. However, the contamination has a detrimental effect even nowadays. Microbial communities are fundamental components of ecosystems playing critical roles in the metabolism of organic matter and xenobiotics as well [4]. Bioremediation that involves the capability of microorganisms to remove pollutants is the most promising, relatively efficient and cost-effective technology [5]. At the locality of the former producer of PCBs Chemko Strážske in eastern part of Slovakia, a large amount of PCBs (mainly the commercial mixture DELOR 103, an equivalent of AROCLOR 1242) is still persisting in sediments and it negatively influences health of the human population. The contaminated area belongs to the so called “old environmental burdens”.

MATERIAL AND METHODS

Determination of ecotoxicity

Lemna minor

Specific inhibitory effects of PCB-contaminated bottom sediments on the growth of the bioindicator *Lemna minor* were measured applying a standard aquatic plant toxicity test. Plants of the species *L. minor* are allowed to grow as monocultures in different concentrations of the tested sample over a period of seven days. The objective of the test is to quantify substance-related effects on the vegetative growth over this period based on the assessment on biomass (total frond area). To quantify substance-related effects, the growth-rate in the test solutions was compared with that of the controls and the concentration resulting in a specified inhibition of the growth-rate was determined and expressed as $I_{(r)x}$.

The toxicity test was performed within seven days in the presence of contaminated sediment. At the beginning of the test and after 2, 4, and 7 days, the images of the beakers were taken for analysis. To evaluate the ecotoxicity of the tested sediments, inhibition of the number of fronds (individual leaf-like structure of a duckweed colony, the smallest unit capable of reproduction) and the frond area were used**.** The test was performed according to the ISO standard 20079 [6] using the Steinberg medium. The biotest was carried out in 150 ml beakers filled with 100 ml of slurry. Preparation of sediment slurries: 10 g of dry sediment was mixed with 100 ml of the Steinberg medium. Ten to 12 fronds (green leaves) were used as the inoculum for each beaker, using only the plants with two or three fronds. Three control replicates and two slurry replicates were used. The data presented are the arithmetic average of the data obtained using the replicates. The tests were carried out in a climatic exposure test cabinet calibrated at 25 ± 2 °C with light intensity adjusted to 6500 Lux. Evaluation of the *Lemna minor* toxicity test was performed using a digital image analysis system Scanalyzer (LemnaTec, GmbH, Germany) at the beginning, and on the 2nd, 4th, and 7th day of cultivation. Inhibition of the frond growth rate (I_r) and frond biomass (I_a) were determined in accordance with ISO 20079.

Microtox

Vibrio fischeri was purchased deep-frozen and liquid-dried from Dr. Lange GmbH (Düsseldorf, Germany) for bioluminescence inhibition assays. Prior to the test, the bacteria were rehydrated using a reconstitution solution provided by the manufacturer.

The 30 min standard bioluminescence inhibition assay was carried out according to ISO 11348-2 [7]. The bacteria suspension and the prepared dilution series of the selected compounds were thermostated in a thermoblock to 15 ± 0.2 °C before testing. The aqueous dilution series were applied to the bacteria suspension in the ratio of 500 + 500 µl. Toxicity of the sediment extracts was evaluated using the bioluminescence bacteria *V. fischeri* (Microtox test) in freeze-dried form (SDI, USA) and activated prior to the test according to the manufacturer's instructions. Since *V. fischeri* is a marine organism, an adjustment of the osmotic pressure of the samples was applied to obtain samples with a 2% salinity using a concentrated salt solution (solution containing 22% of NaCl in deionized water). Light emission of the test organisms obtained by their direct contact with the samples was measured using a luminometer Biocounter LUMAC 1500 (Perstorp, Netherland) within the short exposure time of 15 min. Data processing was performed using the Microtox Omni software (SDI).

Lactuca sativa* var. *capitata

A plastic box with a lid was filled with 100 g of dry sediment wetted to 70 ± 5%. Ten seeds of *Lactuca sativa* var. *capitata* were uniformly distributed on the sediment in the box. The lid was closed and the sample was incubated at 22 °C in an incubator (Sanyo Incubator, USA), for four days in the dark. After 96 hours, the length of all seeds in the samples and control was measured.

Determination of mutagenicity

Ames test

The Salmonella/microsome reversion assay was conducted using the plate incorporation procedure described by Maron and Ames [8]. The Ames test was performed using two bacterial strains of *S. typhimurium*: strain TA98 (CCM 3811) for frame-shift mutations and strain TA100 (CCM 3812) for base-pair substitutions. The test strains were maintained and stored according to the standard procedures [9]. The samples were tested without metabolic activation to detect direct mutagenic compounds. The concentration of the stock solution of PCBs dissolved in DMSO was 5 $g.l^{-1}$.

A mixture of 2 ml of melted Top agar containing 50 µM of L-histidine-biotin, 0.1 ml of bacterial culture (cultivated for 16 h at 37 °C, approximate cell density 2 - 5×10^8 $cells.ml^{-1}$), and 0.1 ml of a solution of the tested compound was poured onto a minimal glucose agar plate and incubated at 37 °C for 48 h in the dark. The number of the his^+ revertants was estimated using a counter. Data points are represented by three separate experiments, each performed in triplicate. Positive (3-(5-nitro-2-furyl)-acrylic acid - NAFA) and negative controls (DMSO) were included in each experiment.

RESULTS

In this work, the evaluation of ecotoxicity of the contaminated bottom sediments using *L. minor* standard bioassay was performed. Inhibition parameters, percentage of growth rate inhibition (% I_r) and the percentage of biomass inhibition (% I_a), were calculated. For the sediment samples from Zemplínska šírava water reservoir, the area inhibition parameters I_r (26.8%) and I_a (22.3%) were higher than I_r (20.8%) and I_a (15.5%) for the number of fronds. For the sediment samples from Strážsky canal, the area inhibition parameters I_r (35.6%) and I_a (30.0%) area were higher than I_r (25.7%) and I_a (18.7%) for the number of fronds. It can be concluded that these stress conditions provided the *L. minor* grow more in the number of fronds than in their biomass on both contaminated sediments.

Ecotoxicity testing included the standard toxicity test known as Microtox using standard marine bacteria *V. fischeri*. To confirm toxic effects of the sediments sampled from Strážsky canal and Zemplínska šírava, sediment extracts were prepared in 2% isopropanol and water, respectively. Toxicity of isopropyl alcohol extracts of the sediments was higher than that of the water ones. The tests with water solutions did not render unambiguous results due to the hydrophobic character of some higher chlorinated PCB congeners. It is obvious that toxicity was expressed more markedly in case of the less polar solvent. Moreover, water extract toxicity detects only the mobile fraction of the contaminant contrary to the organic extract toxicity.

Toxicity of sediments was also evaluated using the contact growth inhibition test of the *L. sativa* roots. Sediment samples of Strážsky canal and Zemplínska šírava water reservoir inhibited the root growth. Results confirm that both sediments contain compounds inhibiting the growth of plant roots (45% inhibition using the sediment from Zemplínska šírava water reservoir and nearly 80% using the sediment sampled from Strážsky canal).

According to the genotoxicity test results, it can be concluded that sediments from Strážsky canal and Zemplínska šírava water reservoir sampled in 2007 were not mutagenic towards *S. typhimurium* TA98 or TA100. In sediments sampled from Strážsky canal in 2008, statistically meaningful medium increase of the induced revertant colonies of *S. typhimurium* TA98 was established. Sediments sampled from Strážsky canal collected in 2009 revealed positive mutagenic effects on *S. typhimurium* TA100, the dosage dependence and the doubling of the revertants number against negative control were observed. There is a high possibility that this sediment contains substances responsible for mutations of *S. typhimurium* TA100.

DISCUSSION

Ecotoxicity of the Strážsky canal sediment samples proved its potential danger to the applied biotests and in comparison with the sediments sampled from Zemplínska šírava water reservoir, they had higher inhibition effects. To summarize all the years of sampling, it can be stated that ecotoxicity did not increase as well as it did not decrease in any sediment sample. Inhibition parameters were stagnant. However, it is important to realize that both sediments have a detrimental impact on biota. Toxicants included in the tested sediments represent a source of adverse effects on life functions of the tested bioindicators. Determination of genotoxicity proved the hazardous potential of the sediments as it increased with time, from year 2007 to 2009. In samples from 2009, the highest genotoxic effects among the tested samples with sediment sampled from Strážsky canal were observed. Thus, it can be assumed that these sediments pose potential ecological and human health risks.

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THE ADAPTATION RESPONSES OF CYTOPLASMIC MEMBRANE ON THE ENVIRONMENTAL STRESS MEDIATED WITH POLYCHLORINATED BIPHENYLS (PCBs) AND 3-CHLOROBENZOIC ACID (3-CBA)

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KEYWORDS
Adaptation responses, bacteria, 3-chlorobenzoic acid, polychlorinated biphenyls, stress

BACKGROUND

Polychlorinated biphenyls (PCBs) are hydrophobic organic compounds that are in the focus of an environmental interest due to their toxicity, persistence, and food chain accumulation ability. They can behave as endocrine disruptors of human and wild life populations. Due to the fact, they are considered as hazardous waste [1]. Slovakia belonged to one of the world´s biggest producers of PCBs. These chemicals were used principally in transformer oils and as electric insulants [2].

Physical and chemical PCB-decontamination technologies in natural environment are costly to introduce. Bioremediation technologies using degradation capacity of bacteria has long been seen as a cost-effective way to eliminate diffusive contamination with PCBs in various environmental matrices, e.g. soils, sediments, and sludges [3].

Successful soil bioaugmentation requires not only application of a strain or a consortium with degradative ability, but also of the microorganisms able to survive in the adverse environment [4, 5, 6]**.** Poor survival of the inoculated microorganisms and low bioavailability of the pollutant are usually the main obstacles to the successful inoculum amendment.

For survival bacteria had to develop efficient adaptation mechanisms in the hostile environment [7, 8]. Hydrophobic organic compounds are known to mainly act on the cytoplasmic membrane causing an increase in the fluidity of the membrane and resulting in significant damage of its physiological function that can lead to cell death [9]. The membrane flexibility and adaptation capability largely determine the survival of the cell. The major constituent of membrane phospholipids are fatty acids. Special membrane desaturases modulate number and position of double bonds of fatty acid chains. Such mechanism plays a critical role in preserving appropriate dynamic state of the membrane bilayer during environmental impact [10]. PCBs affect the saturation of cytoplasmic membrane of various bacterial strains [11]. The correlation between an increase in the degree of saturation of cytoplasmic membrane and increased tolerance toward the toxic compounds was described by Heipieper et al. [12]. Due to this fact, the cytoplasmic membranes become more resistant to strong fluidizing effect of aromatic compounds. In bacteria, only the energy-dependent *de novo* biosynthesis of saturated fatty acids allows the increase in the degree of saturation, which may also be the reason why alteration in the degree of saturation was only observed in growing cells [13]. Another adaptation mechanism, *cis*/*trans* isomerization of unsaturated fatty acids (UFAs), can be observed under growth-inhibiting conditions [14]. Steric differences between *cis* and *trans* configurations reduce membrane fluidity [15].

Some papers described the effect of cyclopropane fatty acids to adaptation to toxic compounds. However, this mechanism is not well understood yet [5, 16]. Lipids of bacteria often contain *iso*- and *anteiso*-branched fatty acids. Branched fatty acids can only be formed by *de novo* synthesis [5]. Transition temperatures of the branched fatty acids are lower for the *anteiso* fatty acids. This difference causes a remarkable change in the fluidity of the membrane when the species of branched fatty acids are changed from one form to another.

The study includes the complex analyzes of the effect of PCBs as potential stress factors on the cell membrane, especially on the profile of fatty acids in the bacterial membrane lipids. Stress effects of PCBs were studied on four bacterial strains *Alcaligenes xylosoxidans* and *Pseudomonas stutzeri*, autochthonous isolates from long-time PCB-contaminated soil [4] and *Ochrobactrum anthropi* and *Pseudomonas veronii* isolated from long-time contaminated bed river sediment. Another goal of the study was to evaluate the adaptation mechanisms of the mentioned strains to 3-CBA, the most toxic PCB biodegradation product.

RESULTS

Differences in adaptation responses to PCB enrichment at the time of inoculation (lag phase) and to PCBs addition to three-day-old culture (stationary phase) were examined.

The addition of PCBs increased the bacterial amount in all strains apart from *P. stutzeri*. PCBs amendment to three-day culture enhanced bacterial growth more than PCBs present in the cultivation medium from the beginning of cultivation (Fig. 1). The highest growth in the presence of 3-CBA was observed for *O. anthropi*. On the other hand, the lowest growth ability after the addition of PCBs or 3-CBa was determined for *P. stutzeri*. The result of lipid accumulation corresponded with that obtained for growth inhibition. In *P. stutzeri* the lipid accumulation exceeded control value when PCBs (1.6 times over control) and 3CBA (4 times over control) were added to three-day-old culture. Higher lipid accumulation was a consequence of adverse environment. The accumulation in *O. anthropi* after the addition of both organic compounds was lower than in the control experiment which is in accordance with bacterial growth. PCBs added at the beginning of cultivation to *A. xylosoxidans* maintained this parameter almost at the same level as in control. Modification of cultivation medium with both types of the used organic compounds to three-day-old culture of *A. xylosoxidans* decreased the lipid accumulation in biomass. These results indicate that the presence of PCBs was not toxic for this strain or the adaptation responses were efficient enough to provide conditions to maintain cell life.

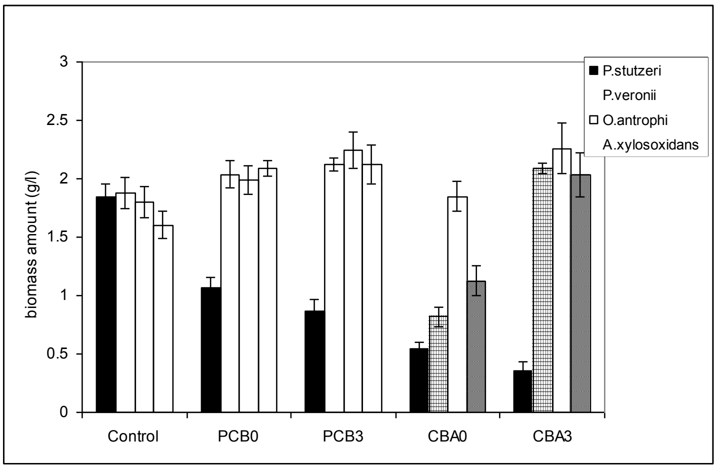

Fig. 1. Biomass amount after six-day cultivation in minimal mineral medium with 100 mg.l^{-1} of PCBs of 3-CBA.

Unsaturation index measured in phosphatidylethanolamine can express the saturation of bacterial membrane [8]. The lower index corresponds to the higher membrane saturation. This index increased after the addition of PCBs to *P. stutzeri* at the beginning of cultivation as well as after the addition of 3-CBA (Fig. 2). Contrarily increase of membrane saturation was observed when we added organic compounds to *O. anthropi* and *P. veronii*. *A. xylosoxidans* decreased membrane saturation after the addition of 3-CBA. This index is dependent to bacterial growth due to the *de novo* synthesis of unsaturated and saturated fatty acids. According to Fig. 1 it could be seen that *P. stutzeri* did not grow after the addition of both organic compounds. This is the reason why the membrane unsaturation index increased.

Trans/cis ratio expresses the cis/trans isomerisation in bacterial membrane. This mechanism is independent to growth conditions and decreases membrane saturation by transformation of *cis* unsaturated fatty acids into correspond *trans* isomers. The *trans/cis* ratio markedly increased after the addition of organic compounds in the experiments with *P. stutzeri* and *O. anthropi* (Fig. 3). Addition to the three-day-old culture resulted in a slight increase of this parameter compared to the addition at the beginning of cultivation. *Cis/trans* isomerisation of *A. xylosoxidans* and *P. veronii* was stimulated predominantly in the presence of PCBs added to three-day-old culture. Addition of 3-CBA at the time of inoculation raised the formation of *trans* fatty acids in comparison to the addition to the three-day culture.

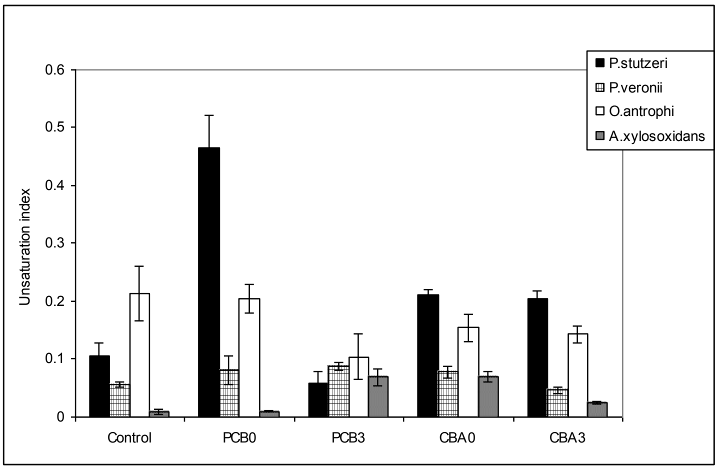

Fig.2. Unsaturation index expressing the percentage abundance of unsaturated fatty acids inphosphatidylethanolamine.

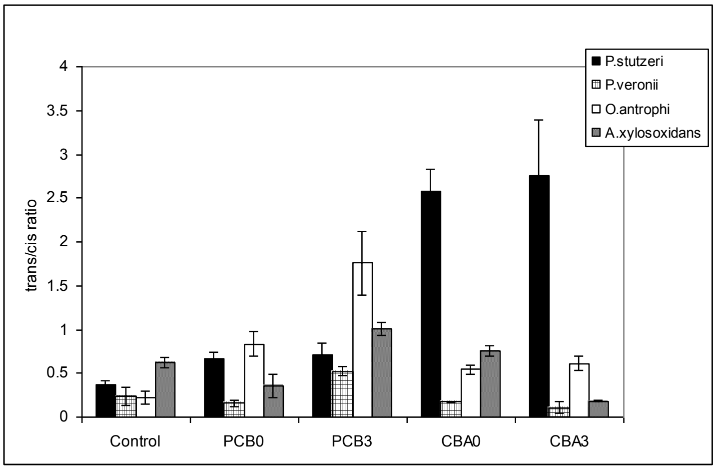

Fig. 3. Trans/cis ratio of unsaturated fatty acids in phosphatidylethanolamine.

Anteiso/iso ratio decreases when bacterial cell needs to increase membrane saturation. The stimulation of this mechanism could be observed with *P. stutzeri* after the addition of both organic compounds (Fig. 4). The lower *anteiso/iso* ratio was observed when PCBs or 3-CBA were added at the beginning of the cultivation. Similar results were obtained in the experiments with *P. veronii*. The ratio decreased after the addition of both tested organic compounds at the time of inoculation. The 3-CBA addition revealed stronger effect on this adaptation mechanism compared to the effect of PCBs for both *Pseudomonas* species. The increase in production of *anteiso* isomers compared to *iso* fatty acids was observed in *O. anthropi* only when 3-CBA where added at lag phase. Similar phenomenon was observed in *A. xylosoxidans* in the presence of 3-CBA, however added at the stationary growth phase.

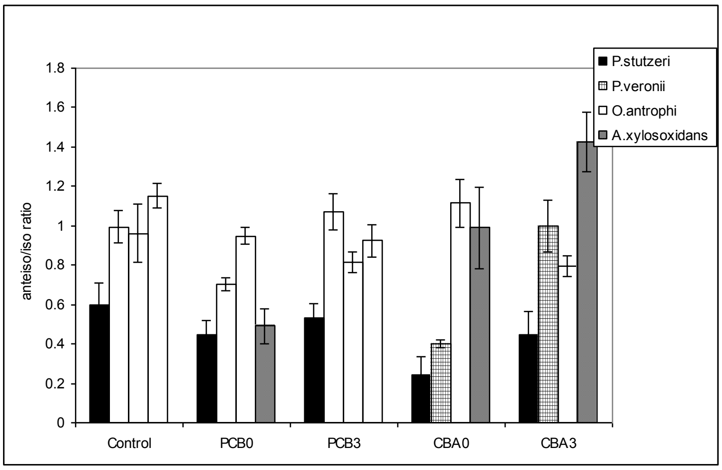

Fig. 4. Anteiso/iso ratio of branched fatty acids in phosphatidylethanolamine.

DISCUSSION

The hydrophobic and toxic compounds act on cytoplasmic membrane leading to its physiological disruption. To counteract this effect, bacteria modify their membrane phospholipids to decrease membrane fluidity and protect the cell core. The used strains revealed different growth sensitivity to the presence of PCBs or 3-CBA. High toxicity of the dead-end product of PCB biodegradation (3-CBA), which is much more toxic than PCBs, was confirmed. 3-CBA increased growth inhibition when added at the beginning of the cultivation. The importance of time contact of xenobiotics during the bacterial growth phase and higher survival ability when the toxic compound was added to stationary growth cells was observed. This observation indicates that the addition of toxic organic compound at the stationary growth phase is more appropriate (less toxic) than at the lag phase.

The adaptation responses and growth ability in both *Pseudomonas* strains were similar. The most adapted strains were identified as *Ochrobactrum anthropi* and *Alcaligenes xylosoxidans*. These strains increased the membrane saturation, cis/trans isomerisation as well as iso/anteiso ratio under the adverse conditions and were able to survive in the contaminated environment that gives them the highest potential for further bioaugmentation experiments.

ACKNOWLEDGEMENT

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NEW TECHNOLOGICAL APPROACH FOR THE PERSONAL MICROCLIMATE COOLING PROCESS IN THE HIGH TOXIC CONTAMINATED SITES

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KEYWORDS
Chemical protection, personal protective equipment, physiological compliance, heat stress, cooling systems.

ABSTRACT

The present study was conducted in order to evaluate efficiency of a different personal body cooling system based on PCM and its effects on CBRN service solders psycho-physiological suitability during exertional heat stress in hot environment and contaminated areas. Performed results are based on conducted examinations in climatic chamber in the Military Medical Academy Institute of Hygiene in Belgrade. Ten male solders-volunteers were subjected to tests on 40 °C temperature and simultaneously to physical effort caused by walking on treadmill at a speed of 5 km/h. After that, they were subjected to realize specific activities in the gas chamber. Tests were performed with solders of middle ages and similar anthropometric parameters, in cases of wearing CBRN isolating protective suit without any cooling system and using several different cooling vests. As a physiological strain indicator has been determined: mean skin temperature (Tsk), tympanic temperature (Tty) and heart rate (HR). Results confirmed that cooling vest under protective suit was able to attenuate the physiological strain levels during specific risk tasks, when compared to identical exposures without the adequate cooling system.

INTRODUCTION

The needed thermal insulation of clothing systems mainly depends on the physical activity and on the surrounding conditions (temperature and relative humidity). The amount of heat produced by humans depends a lot on the physical activity and can differ from 100 W while resting to over 1.000 W during maximum physical performance. At extreme activity, which is often a case with winter sports, the body temperature rises with enhanced heat production. To make this increase within a certain limit, the body perspires in order to withdraw energy from the body by evaporative cooling. If the thermal insulation of the clothing is decreased during physical activity, a part of the generated heat can be removed by convection, thus the body is not needed expected to perspire so much. The quality of insulation in a garment in terms of heat and cold will be widely managed by the thickness and density of its component fabrics. High thickness and low density make insulation better. It is observed in many cases that thermal insulation is offered by air gaps between the garment layers. However, the external temperature also influences the effectiveness of the insulation. The more extreme the temperature, be it very high or very low, the less effective the insulation becomes. Thus, a garment designed for its capability to protect against heat or cold is chosen by its wearer on the expectation of the climate in which the garment is to be worn. Though, a garment produced from a thick fabric will have more weight, and the freedom of movement of the wearer will be restricted. Clearly then a garment designed from an intelligent fabric, whose nature can change according the external temperature, can offer superior protection. However, such a garment must be comfortable for the wearer.

Contemporary needs of military forces request the best possible physiological suitability and comfort of soldiers during accomplishment of missions and tasks in different conditions. With this in mind, different systems for body cooling has been developed, with a main purpose to increase comfort as well as to reduce thermal stress. Cooling system military aplication has some other scientifically valid benefits, such as increased mission duration, decrease in hydration needs, improved mental acuity and maintain physical performance. Even many systems exist today; they generally can by classify in the several basic groups: evaporative cooling products, products based on PCM, compressed air systems, liquid circulation systems and thermoelectric systems. These technical and technological solutions greatly enhance safety and increase the user's physiological suitability, especially during different activities connected with hazard materials (chemical, bilological or radiological).

2. TEST METHODS

2.1. Test subjects

The participants during examination were 10 male professional solders, aged 24 - 32 years (26.8 ± 2.4 years, weight 70 ± 10 kg, and height 182 ± 10 cm).
Before exercises started, the subjects were briefed on the nature of the experiment, its purpose, conditions, safety measures and potential medical risks. Each participant read and signed an informed consent form, in accordance with standards of medical secure during examination in extreme hot or cold environment.
The procedures performed in the present study corresponded to the standards of thermal strain evaluation by psychological measurements.

2.2. Cooling systems

This study focus is to research efficiency of the cooling vest type based on PCM, air ventilation and systems with tubes and compressor. The main goal was to test effects of cooling vest under CBRN protective suit on psycho-physiological suitability during physical effort in hot environment. We hypothesized that vest wearing will alleviate solders physiological strain and will extend so far limited time of stay under isolating protective equipment, in extremely hot conditions. Also, it will increase ability of military personnel to successfully complete any mission in possible chemical, biological or nuclear threats.

COOLING VESTS BASED ON PHASE CHANGE MATERIAL	
ARCTIC HEAT COOLING VEST *(www.arcticheat.com.au)* **Producer:** *Arctic Heat Pty Ltd, Burleigh Heads 4220, Australia.* **Sizes:** S, M, L, XL, XXL, 3XL, 4XL, 5XL. **Cooling effects**: Original pack vest (non-activated) contains crystal balls incorporated into textile packets. By initial soaking in water (activation), crystals swell into gel form, which has ability to keep constant temperature for a long time. **Preparation process** comprise the following simple steps: initially soaking in water for 15 minutes, removing, grabbing top and bottom of vest and gently twisting in opposite directions to remove excess water, then finally hanging to dry. For the cooling effects, vest has to be placed in freezer. **Active working time** depends of the preparation. If frozen for 2 hrs or longer it will stay cold for up 2 hrs. The longer period vest placed in the freezer, the longer it will stay cold. **Weight:** 800 g to 1 kg (when correctly activated).	
SWEDE COOL VEST *(www.firstlinetech.com)* **Producer:** *First Line Technology, 3656 Centerview Drive Suite 4, Chantilly, VA 20151, USA.* **Types:** Mesh, Polyester, or Nomex®. **Sizes:** S, M, L, XL, XXL, 3XL, 4XL, 5XL. **Cooling effects**: Usage of PCM "PhaseCore elements", in a form of 22 cartridges installed into special pockets, which provide a cooling effect to the body's core by absorbing body heat. PhaseCore elements (salt mixture sealed inside an aluminum wrapper), have an activation point of 28 °C or 32 °C, depending on the elements type. When the body temperature rises above this point, the elements begin to absorb body heat. When heat is absorbed, the PhaseCore elements provide a comfortable and soothing cooling effect. Special vest preparation is no necessary. Vest recharges at room temperature. **Active working time**: Vests are effective for up to 4 hrs, based on physical activity, body type as well as environmental conditions. **Weight:** 1.9 kg - 2.15 kg.	 
TEXAS COOL VEST™ *(www.texascoolvest.com)* **Producer:** *Texas Cool Vest 7011 Harwin, Suite 290 Houston TX 77036, USA* Duty, Light, Camouflage, Military. **Sizes:** Only one size, adaptable, fits everyone. **Cooling effects**: Usage of 4 two-parts "cooling packs", inserted into specially designed packets inside the vest. Cooling packs has special ability to freeze on 32 °F (18.3 °C), which automatically becomes capable to absorb excess body core temperature. Garment is designed to keep wearer's core temperature from rising at	

the "normal" rate of associated with physical activity and/or exposure to heated environments. **Preparation:** Packs have to be removed from packaging material and either submerges completely in ice water for 20 minutes or place flat without stacking in a freezer for about 1 hour. When packs are fully charged (completely solid), they should be inserted into garments internal pockets. **Active working time**: Cooling duration will vary due to application, environment and physiological variables. Cooling packs should be removed for regeneration once they are 90 % or more clear liquid.	
COOLING VESTS WITH AIR VENTILATION	
SWOUT® (*www.eng.bluechersystems.com*) **Producer:** BLÜCHER SYSTEMS® GmbH, Van-der-Upwich-Str. 37, 41334 Nettetal, Germany. **Types:** Standalone, with SK1 vest. **Cooling effects**: Swout® is an innovative ventilation shirt designed to provide the wearer with a comfortable and even body climate. The air that is blown into the system is neither dried nor cooled down. The Swout® system simply encourages evaporation so that the body can carry out its natural function of cooling itself via the evaporation of perspiration. Special preparation is no need. It can be worn under all kinds of clothing which tend to keep body heat trapped close to the skin. **Weight:** under 500 g.	
COOLING VESTS WITH TUBES AND COMPRESSOR	
ASPEN SYSTEMS (*www.aspensystems.com*) **Producer:** ***Aspen Systems, Inc.*** *84 Cedar Hill Street, Marlborough, MA 01752, USA* **Types:** Man-mounted, Vehicle installed, Hand held **Cooling effects**: The miniature refrigeration unit is used to chill a liquid (usually water), which is then circulated to a tube-lined garment worn by the user. A custom-designed digital control system maintains the circulating liquid temperature at the user-selected set point by varying the speed of the compressor. The rotary compressor was originally designed to provide 300 W of cooling in a 38 °C environment. Special preparation in no need. **Weight:** ~ 2.72 kg. **Active working time:** up to 4 hrs (cooling time on batteries).	 
PC SYSTEM DP103 (*www.dskool.com*) **Producer:** *DS Kool Inc. Hy-Tech Plaza II, West 1505 Tianan, Guangdong, China* **Sizes:** One size. **Cooling effects**: Based on chilled water flow through the tube system incorporated into the vest. Water flow process is provided by micro-pump with power source. The temperature is set up between 19-25 °C. **Preparation:** A refrigerator is needed to freeze icebox or cryogen, or any source of ice. Icebox has to be placed inside the bladder, then pour more water till the marked line and close the bladder. Vest tubes merge with a hoses leading to the micro-pump. After connecting micro-pump with power source, user should dress the vest, buckles bags around the waist and starts micro-pump by on/off switch. **Active working time**: 1.5 hrs to 4 hrs (depends on physical effort). **Weight:** 1.1 kg (net weight), or 3 kg (during operational usage).	 

2.3. CBRN personal protective set

During exercises, participants are dressed individual isolating protective equipment, which is used by specialized CBRN military units of the Serbian Armed Forces. Equipment comprises protective overall, protective mask (model with phonic unit), protective gloves and boots.

Protective overall M5, used in this study, is made of polyester textile rubberized at each side with butyl and caoutchouc based compound. Protective capacity of overall to drops of toxic agents is not less than 150 min, after 5 alternative contaminations and decontaminations not less than 105 min. Material does not burn out under the effects of thermal impulse of at least 52 J/cm^2 nuclear explosions for 3.5 s of 30 kT. In the contact with drops of burning napalm compound, the overall doesn't burn out for at least 10 s. The mass of protective overall is about 3 kg. It is functional in the temperature range from -30°C to 50 °C.

2.4. Experimental protocol

Each subject performed two exposures, in full protective equipment with the cooling vest and without it. In both cases, exercises performed under the same climatic conditions (40 °C). Before each test conducted, it was necessary to prepare climatic chamber, treadmill, measurement devices and other equipment. Climatic chamber started minimum one hour before, in order to achieve projected temperature.
Cooling vest preparation has been performed in accordance with procedures, by soaking in water and drying day before, than store in freezer one hour, on examination day.
Each subject was weighed without any equipment before and after every experiment.
Taking in consideration climatic conditions, each test was initially limited on maximum 45 minutes. Criteria for stopping exercise before the mentioned time was: achieving of critical value of the tympanic temperature (39 °C), or heart rate (190 bpm), or participants subjective feeling of unbearable effort.

2.5. Psychological measurements

All temperature measurements from the subjects during every exposure were automatically monitored and recorded in real-time using a physiological data monitoring system (Biopac Systems, Inc. USA). System consist of MP150 acquisition unit, universal interface module (UIM100C) and five skin temperature amplifier modules (SKT 100C), single channel, differential amplifier designed especially for skin and core temperature and respiration flow (rate) monitoring. Tympanic and skin temperature was directly measured by TSD202 Series Temperature Transducers.

The average body skin temperature (Tsk) was determined continually, mesuring of local temperatures on four points, using transdusers types TSD202E and TS202F.

Core temperature was measured on eardrum, as tympanic temperature (Tty), conducting adequate thermo-element TSD202A into the aural channel and investing closer to the eardrum. This measurement was also continually, with recording data every 10 seconds.

Heart Rate was measured and recorded automatically using a Quinton® Q4500 Exercise Test Monitor (Quinton Instruments Company, USA). Continual monitoring was done using monitors that received readings from the heart rate straps that were fastened to each subject (on the chest and bottom of spine). The same device was used for control and handling with treadmill (speed and grade).

The test analysis was performed to identify significant difference ($p < 0.05$) between the two exposures: in CBRN protective suit with and without cooling system, for the measured and calculated variables: Tty, Tsk; HR, sweat rate, for the same climatic conditions (40 °C).

3. RESULTS

In exercises performing nobody of the solders showed any symptom of the heat attack during or after test, or any disturbances related to serious types of a heat illness. Average tests lasting were 25 minutes (case without cooling system), respectively 35 minutes (with a cooling vest). Exercises were stopped in a most of cases due to subjective assessment of intolerable effort (92 %), while in less number of cases because of achieving limitary value of tympanic temperature (8 %).

Tab. 1. Comparison of the mean values (±SD) from 10 subjects of tympanic temperature (Tty), average skin temperature (Tsk), heart rate (HR) for temperature and heart rate during EHST

Parameters	**NOCOOL, 35th min, 40 °C**	**With cooling, 45th min, 40 °C**			
		A	**S**	**T**	**O**
Tty	38.88 ± 0.12	38.6 ± 0.18	38.85 ± 0.14	38.97 ± 0.08	38.9 ± 0,09
Tsk	38.22 ± 0.26	37.9 ± 0.22	38.20 ± 0.14	37.78 ± 0.18	38.37 ± 0,11
HR	170 ± 14	162 ± 12	166 ± 15	160 ± 12	173 ± 10

Body skin temperature

Comparable reviews of body skin temperature values with a cooling system and without it are displayed in figure 1.

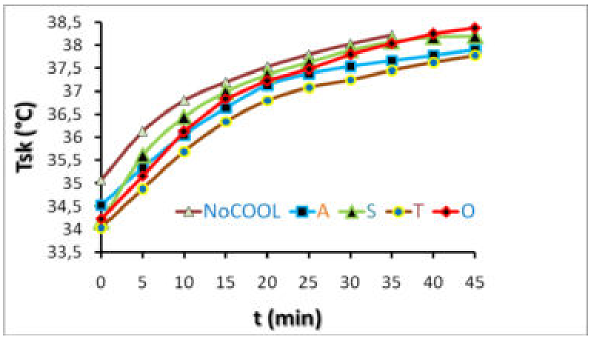

Fig. 1. The mean body skin temperature of all test subjects

Tympanic temperature

Comparable reviews of tympanic temperature values with a cooling system and without it are displayed in figure 2.

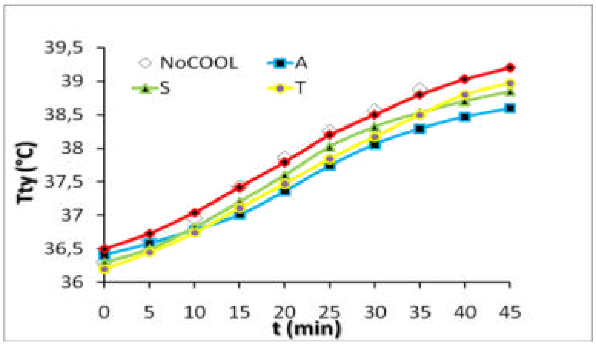

Fig. 2. The mean tympanic temperature of all test subjects

The mean tympanic temperature for all group without vest going from 36.3 °C to 38.63 °C, considered for the maximum exercise time 25 minutes. In case with cooling vest, after the 5th minute temperature began to grow noticeably slower, so in 2th minute was lower for 0,44 °C.

Heart rate

Comparable reviews of heart rate values with a cooling system and without it are displayed in figure 3.

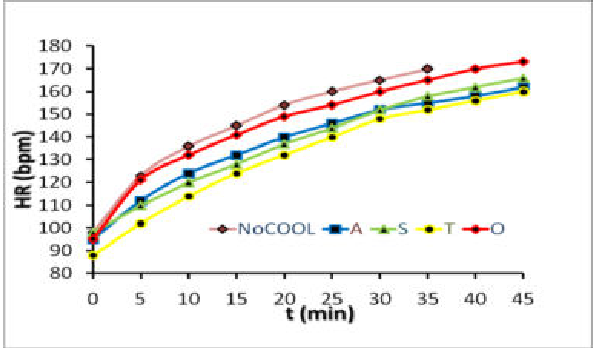

Fig. 3. The mean heart rate values of all test subjects

4. CONCLUSION

Usage of personal body cooling systems under the CBRN protective equipment significantly improves physiological suitability of solders which conduct tasks and missions in complex field conditions, combined with high outside temperature and highly toxic contamination.

The evaluation of different cooling system in this study found two important conclusions: in case of wearing cooling vest, body core temperature (measured through tympanic temperature) grow slower, and mean body skin temperature is significantly lower. Moreover, heart rate values and subjective assessment of comfort levels point to the much expressed solders physiological stability, which is very important result from the aspect of confidence and efficiency in fulfilling the given military missions.

From the CBRN service point of view, the most important result of the whole study is confirmation of established hypothesis that cooling vest application under the protective equipment can extend limited time of stay in hot and CBRN environment.

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ADSORPTION AND OXIDATION OF AS SPECIES IN MODEL BIO-MINERAL SYSTEMS

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KEYWORDS
Arsenic, toxiticy, adsorption, oxidation, iron minerals, microrganisms

ABSTRACT

Special ternary bio-mineral systems, consisting of iron minerals (synthetic goethite and magnetite), bacteria cells of *Ancylobacter dichloromethanicus* As3-1b strain (facultative chemolithotrophic arsenite-oxidizing bacterium) and arsenic salts solution, were constructed and processes of arsenic species adsorption and oxidation were studied. For determination of arsenic species, adsorbed on the surface of the minerals, desorption experiments were carried out also. Results showed that goethite and magnetite effectively adsorbed As salts in non-exchangeable forms. After adsorption by the minerals As(III) partly oxidized to As(V). In the presence of microorganisms added to the mineral before As solution, adsorption of As salts by the minerals decreased sufficiently. In constructed bio-mineral systems *Ancylobacter dichloromethanicus* showed more low oxidation ability in comparison with chemical oxidation on the mineral surfaces.

INTRODUCTION

High toxicity and increased appearance of As in the biosphere triggers public and political concern. Arsenic has been introduced in increasing quantities into the biosphere through past usage of arsenical pesticides and the release of As through mining activities. Ingestion of As through water is the primary cause of As poisoning in humans.

The two most commonly occurring forms of As in the environment are As (V) and As (III), present as the oxyanions arsenate (AsO_4^{3-}) and arsenite (AsO_3^{3-}), respectively. At pH of soil solutions arsenites present in them, mainly as H_3AsO_3 and $H_2AsO_3^-$, because pKa values of arsenious acid are high ($pKa_1 = 9,2$ and $pKa_2 = 12,7$). Arsenates present in the form of arsenic acid anions: $H_2AsO_4^-$ and $HAsO_4^{2-}$($pKa_1 = 2,3$, $pKa_2 = 6,8$ and $pKa_3 = 11,6$). Since the kinetics of redox transformation of arsenic compounds is relatively slow, there are compounds of As (V) and As (III) in soils at the same time (Masscheleyn et al., 1991).
Their high charge density and large surface area, as well as the frequent disorder and poor crystallinity of the particles, make iron minerals essential sorbents of trace elements soils (Perelomov et al., 2011). Because of the variable surface charge, which depends on the pH, they are capable of adsorbing elements in both the cationic and anionic forms.
A mobility of arsenic depends on the physical and chemical properties of soils, the leading of which, apparently, is the acidity of the soil solution (Goldberg, 2002). Compounds of As (V) are less toxic to organisms than As (III) compounds (Penrose, 1974), and oxidation of the latter can be seen as a process of detoxification of arsenic. Oxidation of arsenic compounds can be made by chemical agents and special strains of microorganisms.

The aim of this study was to investigate the adsorption characteristics of As (III) and As (V) compounds, as well as the oxidation of arsenite by goethite, magnetite and in bio-mineral systems consisting of these minerals and cells of bacterial strain *Ancylobacter dichloromethanicus* As3-1b.

MATERIAL AND METHODS

Goethite (α-FeOOH) was synthesized according to the method described by Atkinson et al. (1967), by addition of 200 ml of 2.5 mol l^{-1} KOH to 50 g of $Fe(NO_3)_3{\cdot}9H_2O$ in 820 ml of water until a pH near 12 was reached. The precipitate was washed with deionized water, dialyzed until free of ions, freeze dried and lightly ground to pass through a 0.16 mm sieve. The mineralogy of the iron precipitation product was studied by X-ray diffraction (XRD) analysis and trasmission electron microscopic observation. The XRD pattern showed peaks at 0.418, 0.269 and 0.245 nm, which are characteristic of goethite, but microscopic electron observation showed presence of goethite crystals (mainly) together with some short-range ordered materials. The sample showed a specific surface area of 122 m^2/g and a point of zero charge (PZC) of 8.20. Magnetite (Fe_3O_4) was obtained by oxidation in air special commercial product - NANOFER 25 (NANOIRON, Czech Republic), in which the content of Fe

(0) was about 85% dry weight. The specific surface area of the material according to the manufacturer is more 25 m^2/g.

Ancylobacter dichloromethanicus As3-1b is Gram-negative asporogenous catalase-positive rod-shaped movable Proteobacteria (Andreoni et al., 2012). Strain was isolated from the agricultural soil (Tuscany, Italy) contaminated by arsenic as arsenopyrite. In the soil concentration of the element reached 250 mg/kg.Microbial biomass was obtained by growing the bacterial cells in liquid LB medium. Separation of microorganisms and medium was accomplished by centrifugation at 9000 rpm for 15 minutes, followed by washing and similar centrifugation.

Stock solutions of As (III) and As (V) salts were obtained from $NaAsO_2$ and $Na_2HAsO_4x7H_2O$ (Sigma-Aldrich). For sorption experiments 0.1 g of the corresponding mineral and 20 ml of solution with a concentration of 0.3 mmol, 0.6 mmol, 0.9 mmol (or 60, 120 and 180 mmol/kg of mineral) were used. In experiments with microorganisms, the bacterial count was $0.5x10^9$ cells/ml. The mineral was equilibrated with 5, 10 and 15 ml of physiological solution for 17 hours without shaking. After that 15, 10 and 5 ml of 1.2 mmol solution of arsenic salts were added to experimental vessels to reach the studied concentrations. The experiments were carried out at initial pH of the sorption solution 7.2. After the experiment the solid and liquid phases were separated by centrifugation at 9000 rpm for 15 minutes, followed by filtration of the solution through a filter with a pore diameter of 0.22 µm. Washing the solid phase was carried out by shaking with 5 ml of distilled water followed by centrifugation at 9000 rpm for 10 minutes.

Desorption of arsenic compounds was performed by adding 10 ml of 0.1 M NH_4OH to the washed pellet and by shaking for 4 hours. At the end of the procedure the solid phase was separated from the liquid by centrifugation at 9000 rpm for 15 minutes, followed by filtration of the solution through a filter with a pore diameter of 0.22 µm. Determination of arsenic in solution was performed spectrophotometrically (Dhar et al., 2004).

RESULTS AND DISCUSSION

Goethite effectively absorbs arsenic salts: adsorption of As (III) on the mineral ranged from 66 to 82%, the absorption of As (V) – from 52 to 82% from added (Fig. 1). Several authors suggested that arsenites are more mobile than arsenate in the environment (Tamaki and Frankenberger, 1992). In our experimental conditions (pH 7.2), there were no differences in the absorption of arsenic III and arsenic V at concentrations of 60 and 120 mmol/kg, but at concentration of 180 mmol/kg more As (III) was absorbed from the solution. When the mixture of As (III) and As (V) was added (each salt at concentration of 60 mmol/kg) the total amount of arsenic absorbed by goethite was not significantly changed in comparison with additions of 120 mmol As (III) or 120 mmol As (V) separately. Grossl et al. (1997) proposed that the adsorption of arsenate to α-FeOOH involved a two-step ligand exchange reaction by which an inner-sphere bidentate surface complex is formed. Sun and Doner (1996) established that As (V) and As (III) replace two singly coordinated surface OH groups on α-FeOOH to form binuclear bridging complexes. As desorbing agents we studied 0.005 M and 0.05 M $(NH_4)_2SO_4$, 0,1 M NH_4OH, 0,2 M NH_4-(Ox)-buffer in 0,1 M ascorbic acid (pH 3,25). A solution of 0.1 M NH_4OH showed the best desorbing properties. According to the scheme of sequential extractions of Wenzel et al. (2001) ammonium hydroxide extracts specifically adsorbed forms of arsenic.

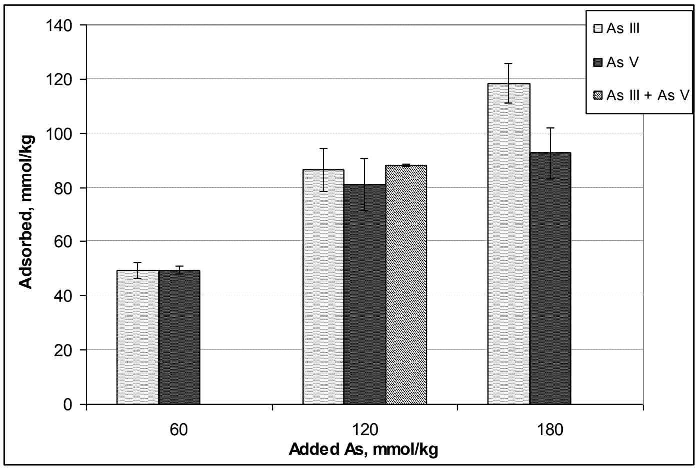

Fig. 1. Adsorption of As salts by goethite at pH 7.2

After removing by ammonium hydroxide specifically adsorbed arsenic species from 80.9% to 92.1% of the absorbed element retained on the goethite surface (Fig. 2). There were no differences in the strong retention of arsenic at additions of As (III) or As (V). Similar results were obtained for magnetite also.

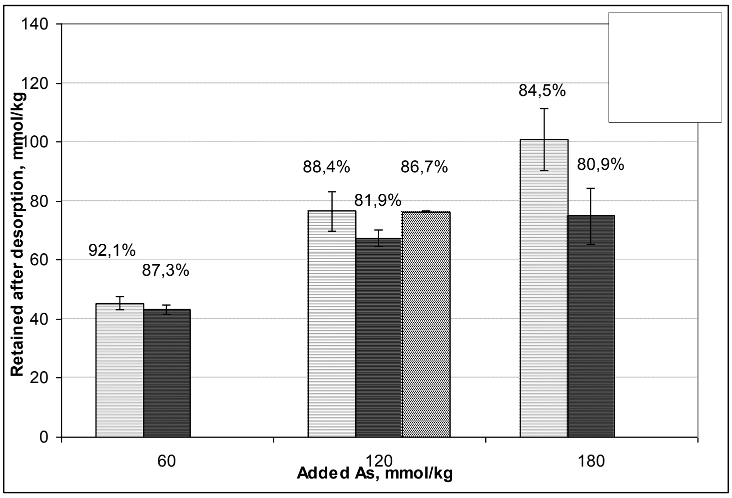

Fig. 2. Amount of As retained by goethite after desorption

On average 87.4% of the arsenic at the treatment of 60 mmol/kg, 36.1% at 120 mmol/kg and 14.8% at 180 mmol/kg desorbed in the form of As (V); so chemical oxidation of arsenite to arsenate on the surface of goethite was observed (Fig. 3). Our results are consistent with (Wilkie and Hering, 1996; Sun et al., 1999), which indicated the possibility of oxidation of As (III) by iron oxides. Lievremont et al. (2003) showed that the mineral chabazite (17.6% of Al, 4.1% of Fe_2O_3, 0.12% of MnO and 0.57% of TiO) chemically oxidized 50% of arsenite at 1 mmol for 48 hours. At the same time Manning and Goldberg (1997) showed absence of arsenite oxidation on the surface of synthetic goethite.

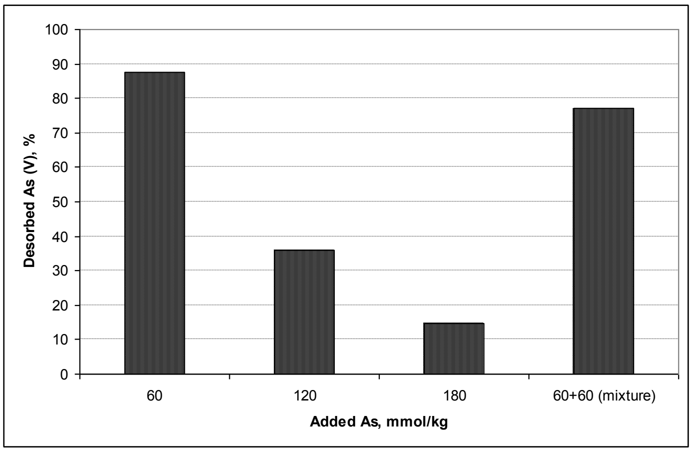

Fig. 3. Desorption of As (V) from goethite after adsorption of As (III) and mixture of As (III) and As (V)

Detailed analysis of the compounds adsorbed on the surface of magnetite (Fig. 4) from the mixture of As (III) and As (V) at concentrations of 0.3 mmol indicates preferential As (III) adsorption by the mineral. However, mainly As (V) compounds were desorbed from the surface and desorbed As (III) reached about 16% from the total amount of desorbed element only. Thus, the reason for the low recovery of arsenites may be their chemical oxidation on the surface of iron minerals.

Andreoni et al. (2012) showed a high efficiency of biological oxidation of arsenite by strain *Ancylobacter dichloromethanicus* As 3-1b, cultivated in BBM medium, where as an additional source of carbon $NaHCO_3$ was used. In the presence of 0.01% yeast extract microbial growth and oxidation of arsenite significantly increased.
However, in our experimental solutions in the absence of additional carbon sources oxidation of arsenite was expressed very poorly. At initial concentration of arsenite in the solution of 0.3 mmol and *Ancylobacter*

dichloromethanicus cells concentration of 0,5x10^9 cells/ml less than a quarter of introduced arsenic oxidized to arsenates within 46 hours. Possible causes of low biological oxidation may be a lack of available for the microorganisms forms of carbon in the solution, and the absence of induction of arsenite oxidase in the microbiological medium for the bacteria cultivation by adding As (III) salts (Lievremont et al., 2003).

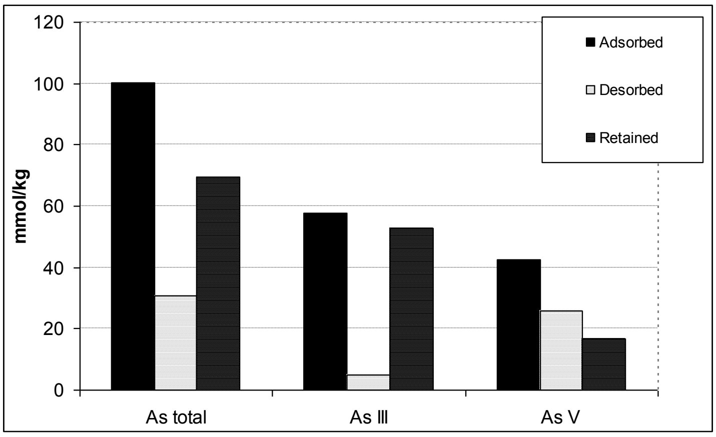

Fig. 4. Adsorption and desorption of As compounds at additions 0.3 mmol As (III) and 0.3 mmol As (V)

To study the role of mineral and biotic components in an adsorption and oxidation of arsenic special model ternary bio-mineral systems were used. These systems include: 1) solution of arsenite; 2) goethite or magnetite; 3) *Ancylobacter dichloromethanicus* cell suspension. Appropriate mineral and microbial suspension were incubated together for 17 hours and then solution of As (III) was added to the system for 4 hours. Results of sorption and oxidation of arsenite in bio-mineral systems (for goethite at As concentration of 0.3 mmol and for magnetite at concentration of 0.6 mmol) are shown in Fig. 5 and 6. In the presence of microorganisms adsorption of arsenite decreased on the surface of goethite and magnetite.

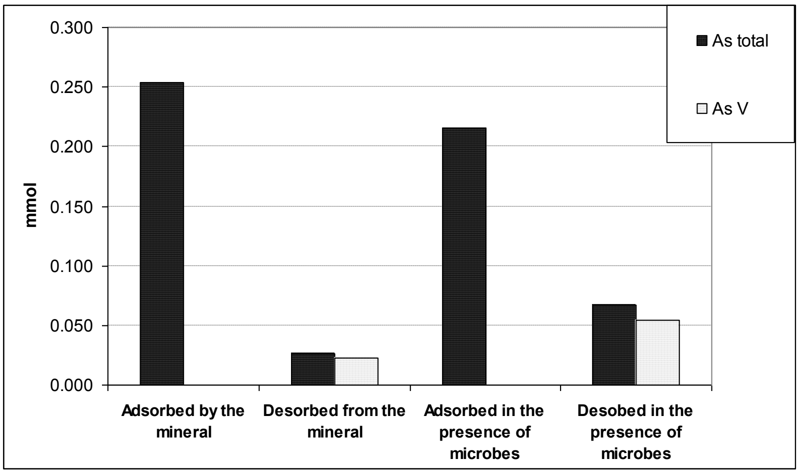

Fig. 5. Adsorption/desorption of As in bio-mineral system included goethite at 0.3 mmol of As

Previously, we have shown that electrostatic interactions play sufficient role in the interactions between minerals, microorganisms and trace elements in bio-mineral systems (Perelomov and Yoshida, 2008). Surface of iron minerals has a positive charge at pH below points of zero charge. Points of zero charge for cell walls of most microorganisms are localized at pH of 4.5 or lower. Thus, at pH 7.2 there are electrostatic interactions between positively charged mineral surfaces and negatively charged cell walls and precipitation of cells on the surface of goethite and magnetite. The precipitation can lead to masking sorption positions on the surface of minerals and partial reduction of their positive charge. In addition, bacterial cells adsorbed on the surface of goethite and magnetite can repel like-charged arsenite ions (including hydrated). These processes lead to the decrease in absorption of arsenic compounds on the surface of minerals.

In the case of goethite, microorganisms reduce the bound strength between arsenic and mineral surface - the amount of desorbed arsenic increases both in absolute values and as a percentage from amount of absorbed element in the bio-mineral system. Main part of the desorbed arsenic are arsenates, the amount of which increased in comparison with desorption from the pure mineral surface. In the case of magnetite, amount of desorbed arsenic is increased in relation to amount of the element, absorbed in the bio-mineral system. At these conditions amount of desorbed As (V) even decrease that proves significant chemical oxidation of arsenites.

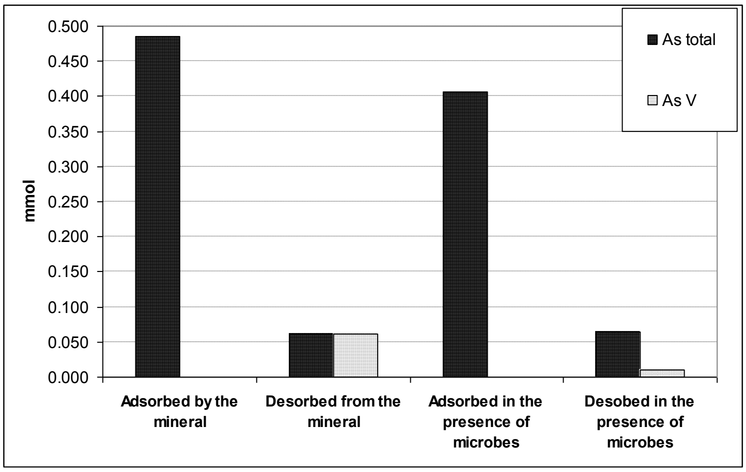

Fig. 6. Adsorption/desorption of As in bio-mineral system included magnetite at 0.6 mmol of As

CONCLUSIONS

Thus, goethite and magnetite are effective sorbents of arsenic (III) and arsenic (V) compounds and strongly bound them on mineral surface. These iron minerals can be actively used for remediation of contaminated soils and grounds and waste water treatments. After adsorption by iron minerals arsenites partly oxidized to less toxic arsenates. In the presence of microorganisms adsorption of arsenites on the surface of goethite and magnetite decreases, which is satisfactorily described by electrostatic interactions. Without special conditions that are favorable for metabolism of arsenite-oxidizing microorganisms, biological oxidation of As (III) compounds is low and chemical oxidation prevails.

ACKNOLIGEMENTS

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THE CHEMICAL ASPECTS OF THE IN-SITU CHEMICAL OXIDATION (ISCO) OF SOILS FROM CHOSEN ORGANIC COMPOUNDS (PAHs, CHCs)

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KEYWORDS
ISCO, PAHs, CHCs, permanganate, persulfate, gas chromatography-mass spectrometry (GC-MS), head space gas chromatography (headspace/GC), Polish soil quality standards

ABSTRACT

The article presents the chemical aspects of the in-situ chemical oxidation (ISCO) of soils from chosen organic compounds – PAHs (Polycyclic Aromatic Hydrocarbons) and CHCs (Chlorinated Aliphatic Hydrocarbons). It describes the fundamental chemical reactions, which occur during treatment (as an instance treatment of CHCs using permanganate and persulfate was described), the toxicity and physicochemical properties of CHCs and PAHs as well as the laboratory methods that can be used to detect substances in question. Furthermore, the Polish regulation regarding soil quality standards for PAH and CHC is presented.

1. INTRODUCTION - THE BASIS OF ISCO

Treatment of ground-water environment using chemical oxidation methods (ISCO - In Situ Chemical Oxidation) relies on injecting of oxidants into the vadose and /or saturation zone by means of injection wells. Consequently, oxidants react with contaminates, which result in the formation of harmless end products such as CO_2, H_2O and in case of the chlorine-containing substances - Cl_2.
Among the chemical compounds susceptible to ISCO are: BTEX (benzene, toluene, ethylbenzene, xylenes), MTBE (methyl tert-butyl ether), TPHs (total petroleum hydrocarbons), chlorinated hydrocarbons (ethanes and ethenes), PAHs (polycyclic aromatic hydrocarbons), PCBs (polichlorinated biphenyls), phenols, organic pesticides [1].
The most common oxidizers used in ISCO methods are the following: hydroxyl radicals, sulfate radicals, ozone, persulfate, peroxide (Fenton's reagent), permanganates, superoxide ion. In this article the author focused on chemical oxidation of CHCs with permanganate and persulfate. In the case of PAHs and organic pesticides their mechanism is not fully known [1].

2. FUNDAMENTAL CHEMICAL REACTIONS OCCUR DURING TREATMENT OF CHC USING PERMANGANATE AND PERSULFATE

2.1 Permanganate

In chemical oxidation permanganate is most commonly used as a 4% solution of $KMnO_4$ or 40% solution of $NaMnO_4$. Permanganate ion (VII) undergoes the following half-reactions depending on the pH of the environment [1]:

pH<3,5 $$MnO_4^- + 8H^+ + 5\bar{e} \leftrightarrow Mn^{2+} + 4H_2O \quad (1)$$

3,5<pH<12 $$MnO_4^- + 2H_2O + 3\bar{e} \leftrightarrow MnO_{2(s)} + 4OH^- \quad (2)$$

pH>12 $$MnO_4^- + \bar{e} \leftrightarrow MnO_4^{2-} \quad (3)$$

Due to the typical pH of the ground-water environment is in the range of 6.5-8.5 [2], permanganate ion (VII) will undergo reaction no. 2 during oxidation processes of CHC:

Terachloroethen

$$4KMnO_4 + 3C_2Cl_4 + 4H_2O \rightarrow 6CO_2 + 4MnO_{2(s)} + 4K^+ + 12Cl^- + 8H^+$$

Trichloroethen

$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_{2(s)} + 2K^+ + 3Cl^- + H^+$$

Dichloroethen

$$8KMnO_4 + 3C_2H_2Cl_2 \rightarrow 6CO_2 + 8MnO_{2(s)} + 8K^+ + 6Cl^- + 2H_2O + 4OH^-$$

Vinyl chloride

$$10KMnO_4 + 3C_2H_3Cl \rightarrow 6CO_2 + 10MnO_{2(s)} + 10K^+ + 3Cl^- + 7OH^- + H_2O$$

2.2 Persulfate

The most commonly used in remediation is sodium persulfate solution (40%). Although ammonium persulfate is more soluble than the first-mentioned salt (46% solubility), it is not applied due to the formation of ammonia, which affects the change in pH environment.
After dissolution in water, salts dissociated and creates persulfate ion, which undergoes the following reactions depending on the pH of the environment:

pH<3,0 $$S_2O_8^{2-} + 2H_2O + H^+ \leftrightarrow HSO_4^- + HSO_5^- \quad (1)$$

3,0<pH<7,0 $$S_2O_8^{2-} + 2H_2O + H^+ \leftrightarrow 2HSO_4^- + H_2O_2 \quad (2)$$

pH=7,0 $$S_2O_8^{2-} + 2H_2O \leftrightarrow 2HSO_4^- + \frac{1}{2}O_2 \quad (3)$$

pH>13 $$S_2O_8^{2-} + OH^- \leftrightarrow HSO_4^- + SO_4^{2-} + \frac{1}{2}O_2 \quad (4)$$

Addition of iron salts (II) or raising the temperature dramatically increases the strength of persulfate oxidation, due to formation of highly reactive sulfate free radicals according the following reactions:

Initiating reactions:

$$S_2O_8^{2-} \rightarrow 2SO_4^{-\bullet}$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow 2SO_4^{-\bullet} + Fe^{3+}$$

$$S_2O_8^{2-} + RH \rightarrow SO_4^{-\bullet} + R^\bullet + HSO_4^-$$

Chain elongation:

$$SO_4^{-\bullet} + RH \rightarrow R^\bullet + HSO_4^-$$

$$SO_4^{-\bullet} + H_2O \rightarrow OH^\bullet + HSO_4^-$$

$$OH^\bullet + RH \rightarrow R^\bullet + H_2O$$

$$R^* + S_2O_8^{2-} \rightarrow SO_4^{-\bullet} + HSO_4^- + R$$

$$SO_4^{-\bullet} + OH^- \rightarrow OH^\bullet + SO_4^{2-}$$

Chain termination:

$$SO_4^{-\bullet} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-}$$

$$Fe^{2+} + OH^\bullet \rightarrow OH^- + Fe^{3+}$$

$$Fe^{3+} + R^\bullet \rightarrow R + Fe^{2+}$$

$2R^\bullet \rightarrow$ chain termination

3. CHARACTERISTIC OF PAHS AND CHCS

3.1 Polycyclic Aromatic Hydrocarbons

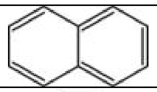
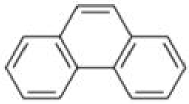
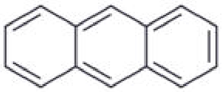
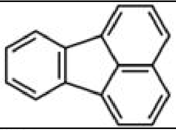
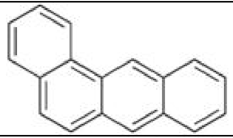
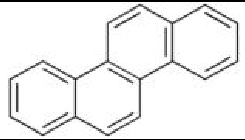
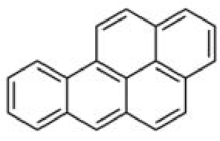
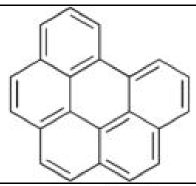
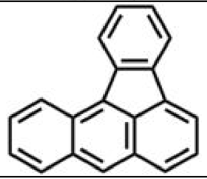
Polycyclic aromatic hydrocarbons (PAHs) are a large group of aromatic compounds. More than 100 PAHs are known. In the natural environment 16 PAHs are the most common [2]. They represent homologies of benzene with the number of rings equal to 2 or more. They consist mainly of carbon and hydrogen atoms, but also nitrogen, sulfur and oxygen. The lightest representative of this group of compounds is naphthalene having two rings (molecular weight – 128,16 g/mol) and the heaviest is coronene having seven rings (molecular weight – 300,36 g/mol) [3].

PAHs have similar physical and chemical properties. In their pure state they form colorless, white, pale yellow or light green crystals. Many of them exhibit the physical phenomenon of fluorescence, which is used in quantitative analyses. PAHs are poorly soluble in water (they are hydrophobic), preferably in organic solvents. Their solubility is in the range from 0,0018 μg/dm^3 to 260 μg/dm^3 in 20-25 ˚C [2]. It grows with temperature, in the range of 5 to 30 ˚C two to five times [4].

PAHs are formed by incomplete combustion of other hydrocarbons and pyrolysis. The main anthropogenic sources of these compounds are: gases from diesel engines (exhaust gases), fumes from furnaces, in which wood, oil, coke, fossil fuels are burn, cigarette smoke, soot and dust, slag, baked foods, smoked cheese, fish and meat products, residues of coal tar, and crude oil, asphalt production, biomass and waste combustion. Natural sources are forest and steppe fires, volcanic eruptions (fumaroles) and hot springs, offshore oil spills, erosion of sediments enriched with organic substances [3]. Light PAHs are less toxic and not carcinogenic. Heavy PAHs are carcinogenic to animals and can be for humans [2, 3].

The basic information regarding PAHs, which are included in Polish Standards regarding soil quality, are presented in the table 1.

Tab. 1. The basic information regarding polycyclic aromatic hydrocarbons

Parameter	CAS no.	Molecular formula	Structural formula
Naphthalene	91-20-3	$C_{10}H_8$	
Phenanthrene	85-01-8	$C_{14}H_{10}$	
Anthracene	120-12-7	$C_{14}H_{10}$	
Fluoranthene	206-44-0	$C_{16}H_{10}$	
Benz(*a*)anthracene	56-55-3	$C_{18}H_{12}$	
Chrysene	218-01-9	$C_{18}H_{12}$	
Benzo(*a*)pyrene	50-32-8	$C_{20}H_{12}$	
Benzo(*ghi*)perylene	191-24-2	$C_{22}H_{12}$	
Benzo(*a*)fluoranthene	203-33-8	$C_{20}H_{12}$	

3.2 Aliphatic Chlorinated Hydrocarbons

The most important aliphatic chlorinated hydrocarbons are tetrachloroethene and trichloroethene. They are the mother products present in the ground-water environment, which break down into cis-and trans-dichloroethene [2].

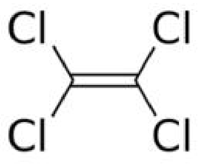
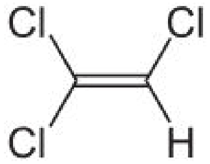
Tetrachlorethene is a colorless liquid with a sweet ether-like odor. The high volatility of this compound makes it rapidly escaping to the atmosphere from groundwater (Boiling point = 121,1 °C). It is very soluble in water (150 mg/dm^3), which is the cause of the high pollution of environment. Its density equals to 1,622 g/dm^3.

Tetrachlorethene was used for "dry" chemical cleaning, for degreasing of metal surfaces, as a solvent for oils, fats, also as a stain remover. In the chemical industry it was used as an intermediate for a numerous organic synthesis. Accordingly, contamination is found mainly in the industrial areas, airports and landfills.

Trichloroethene is a colorless liquid with an odor of chloroform. There are about ten times more soluble in water (1100 mg/dm^3) than tetrachloroethene, causing serious environmental pollution. The high volatility of this compound makes rapidly escaping to the atmosphere from groundwater (Boiling point = 87.2 ° C). It may be formed as a degradation product of tetrachloroethene. Its density equals to1,46 g/dm^3 [2].

The basic information regarding PAHs is presented in the table 2.

Tab. 2. The basic information regarding tetrachlorethene and trichloroethene

Parameter	Tetrachlorethene	Trichloroethene
CAS no	127-18-4	79-01-6
Abbreviations	PCE, PER	TCE, TRI
Molecular formula	C_2Cl_4	C_2Cl_3H
Structural formula		
Molecular weight	165,83 g/mol	131,39 g/mol

4. LABORATORY METHODS USED FOR ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS AND ALIPHATIC CHLORINATED HYDROCARBONS

4.1 Extraction in Dichloromethane and Hexane with Mass Detector - Gas Chromatography-Mass Spectrometry (GC-MS)

The PAHs are known as the "organic microcontaminants", which are present in ground-water environment usually in concentrations of several nanograms; therefore, a major problem is their separation for analysis by extraction with an organic solvent. The most frequently used for this purpose are cyclohexane or dichloromethane or solid absorbents, which are subjected to a further purification from substances interfering in the analysis using gas chromatography [2]. Gas chromatography allows separating of liquid mixtures; nevertheless do not give detailed information about composition. On the other hand the mass spectrometry is reliable only in case of pure substances. The analysis of PAHs in the laboratory are conducted using combination of both methods, which assure obtaining pure extract of PAHs in the first method and detailed information about a quantity and a kind of chemical substance from an extract in the second one. The smallest concentration measurable in the laboratory is 0,01 µg/dm^3 [5].

4.2 Head Space Gas Chromatography (Headspace/GC)

This method is used for analysis of highly volatile substances with a boiling point below 200°C and slightly soluble in water. Gas chromatography with a headspace analysis uses the enrichment of the gas phase in the more volatile substances (VOC - volatile organic compounds, for example aliphatic chlorinated hydrocarbons) which are in equilibrium with a solution in a closed container. Equilibrium gas phase is led directly to the gas chromatograph for separation and analysis. This method has many advantages such as the elimination of the sample preparation or its significantly reduce, the possibility of heating the sample in a dispenser "headspace", which increases the concentration of substances in the gas phase. The precise temperature control allows obtaining repetitive results. Headspace method is based on the Raoult's law, which states that a dependence of a partial pressure “p” of an “i” component in a gas phase depends on its concentration in the liquid mixture [5]:

$$p_i = x_i \cdot p_i^{0}$$

where:
p_i^0 - means the vapor pressure on the pure component,
x_i - mole fraction of an "I" component in the liquid mixture.

4. POLISH STANDARDS REGARDING PAHS AND CHCS CONCENTRATIONS IN SOIL

Laboratory results of soil samples collected in Poland are compared with the permissible concentrations defined in Polish law. The standards for soil and ground quality in Poland are included in the Regulation of the Minister of Environment, published in the Journal of Laws No. 165, item 1359, dated September 9, 2002. According to this, land is regarded as contaminated when the concentration of at least one compounds exceeds the mentioned above standards (with exception of natural high occurrence of the listed substances). Soil standards were established for three groups of lands i.e.:
Group A: land located in protected areas according to the valid Polish Water Protection Act and the Nature Protection laws.
Group B: agricultural areas (with exception of lands under water in ponds and ditches), forest and tree-covered or shrub-covered lands, wastelands, developed and urbanised lands (except industrial and mining lands and areas used for transportation).
Group C: industrial, mining and transportation lands.
All soil quality standards refer to dry soil. The standards within B and C Groups of land are established for three and two soil depths, respectively, which should be consider during soil sampling. Additionally, the permissible values depend on hydraulic conductivity of soils (see table 3).

Tab. 3. Polish soil quality standards regarding PAHs and CHCs

Parameter	Permissible concentration for "Group A"	Permissible concentrations for „Group B" [mg/kg d.w.]					Permissible concentrations for „Group C" [mg/kg d.w.]		
		Depth [m bgl]							
		0-0,3	0,3-15,0		>15		0 - 2	2 - 15	
		Hydraulic conductivity [m/s]							
		-	To 10^{-7}	Below 10^{-7}	To 10^{-7}	Below 10^{-7}	-	To 10^{-7}	Below 10^{-7}
Polycyclic Aromatic Hydrocarbons (PAHs)									
Naphthalene	0,1	0,1	5	20	10	40	50	10	40
Phenanthrene	0,1	0,1	5	20	10	40	50	10	40
Anthracene	0,1	0,1	5	20	10	40	50	10	40
Fluoranthene	0,1	0,1	5	20	10	40	50	10	40
Benzo(a)anthracene	0,1	0,1	5	20	10	40	50	10	40
Chrysene	0,1	0,1	5	20	10	40	50	10	40
Benzo(a)pyrene	0,02	0,03	5	10	5	40	50	5	40
Benzo(ghi)perylene	0,1	0,1	10	10	5	40	50	5	100
Benzo(a)fluoranthene	0,1	0,1	5	10	5	40	50	5	40
Sum of PAH	1	1	20	40	20	200	250	20	200
Aliphatic Chlorinated Hydrocarbons (CHCs)									
Aliphatic Chlorinated Hydrocarbons (single)	0,01	0,01	0,1	5	1	10	5	1	20
Aliphatic Chlorinated Hydrocarbons (sum)	0,01	0,01	0,15	7	3	40	60	2	40

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THE ROLE OF BIOCHAR IN THE PHYTOREMEDIATION OF METAL/METALLOID CONTAMINATED SOILS

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KEYWORDS

Heavy metals, remediation, biochar, contaminated soils, uptake

ABSTRACT

Biochar has been evaluated for its role in improving soil quality and sequestering carbon, with much less attention paid to soil clean-up and remediation. In the following study a hardwood biochar and greenwaste compost alone and in combination were mixed with two contaminated soils (As, Cd, Cu, Pb and Zn) from former industrial sites and, following environmental exposure, pore water was collected and ryegrass (L. perenne L. var. Cadix) germinated to determine the amendments affects on i) solubility/mobility of the elements and ii) uptake and phytotoxicity to ryegrass.

Biochar was most efficient at reducing Cd and Zn in pore water, decreasing phytotoxicity to ryegrass, but mobilized small concentrations of As. Copper in pore water was also reduced by a decrease in dissolved organic carbon (DOC) and co-mobility. Greenwaste compost was more efficient for immobilizing Pb than biochar alone but combining greenwaste compost and biochar provided the best conditions for ryegrass growth and yield because of the immobilization of metals and the input of N and P from compost. Despite some reductions in ryegrass shoot concentrations of metals after amendment, the large biomass increase raised harvestable amounts of the metals, increasing food chain transfer potential. An assessment should therefore be made as to whether maximum reductions in plant concentrations or maximum reduction in harvestable amounts of metals are required to ensure amendments may be suitably deployed to maximize their effects.

INTRODUCTION

Significantly elevated levels of inorganic pollutants exist in soils from previously heavily industrialised areas. Element solubility, bioavailable and mobility influence the extent to which plant uptake and potential transfer are impacted. The use of soil amendments can effectively reduce water-soluble fractions, and hence transfer, but the effects are often element and soil specific.

Biochar is a low density, charred, biomass derived soil amendment with already proven benefits to soil fertility (Novak et al, 2009) whilst its high C content makes it an attractive option for enhancing C storage. The results of two recent field and laboratory studies in the UK are compared with the aim of establishing whether biochar, or biochar in combination with green waste compost can immobilize As, Cd, Cu, Pb and Zn, reducing phytotoxicity and potential risk to food chain transfer.

MATERIALS AND METHODS

Soil was collected from two sites, in each case from the upper 15 cm soil depth; the first from an embankment separating two canals in Kidsgrove (KD), Staffordshire, UK (Lat/Long: 53°05’23.0” N, 02°15’05.7” W) and the second from a barren area within mature woodland at the Alderley Edge (AE) former copper mine site in Cheshire, UK (Lat/Long: 53°17’48.19” N, 02°12’42.68” W). Heavy industrial use and associated pollution legacy are features of both sites. At Kidsgrove the soil was primarily As, Cd and Zn polluted, whilst at Alderley Edge elevated Cu and Pb concentrations were prevalent (Table 1).

Soil was mixed with greenwaste compost, biochar or a combination of the two amendments at rates of 30% amendment to 70% soil (by volume) into triplicated 1 litre pots. Following an equilibration period, soil pore water was collected from each pot at regular intervals during environmental exposure, by Rhizon samplers. Pore water was analysed for dissolved organic carbon (DOC) by a Shimadzu TOC-VE instrument (Japan) and As, Cd, Cu, Pb and Zn concentration by ICP-MS (Thermo Scientific, USA). For AE, soil was sown with 2 g of ryegrass seed (*L. perenne* L. var. Cadix). The ryegrass biomass was harvested 2, 3 and 4 months after germination with stainless steel scissors, shoots were washed in deionised water, oven-dried at 45°C for 24 h then ground in a Cyclotec 1093 sample mill. Aliquots of the ground material were weighed (0.2 g) into digestion vessels, 10 ml of 14 M Analar grade HNO_3 added, microwaved and analysed by the same ICP-MS as above. For KD a simple phyto-toxicity test was employed using *L. perenne* L. var. Cadix. Triplicate petri dishes were filled with 30g of soil collected after 60 days field exposure and watered to saturation. After 6 h, 20 seeds were placed over the soil surface. Petri dishes were incubated for 96 h under darkness at 28 ºC and 60 % relative humidity in environmental chambers (Conviron, USA). Successfully emerged plants (those with shoots longer than 1 cm) were counted and the emergence success was calculated as a percentage of the 20 seeds applied to the surface of each soil whose shoots exceeded 1 cm length.

RESULTS

The pH of both soils was similarly acidic, whilst the organic matter content of KD soil was 4-fold greater than AE (Table 1).

Tab. 1. Soil characteristics of each site (mean n= 3)

Site	KD	AE
Organic Matter %	16.5	4.3
pH	5.5	5.4
Pseudo total (mg kg-1)		
As	96	-
Cd	119	-
Cu	-	603
Pb	-	20703
Zn	249	-

At KD, where Cd and Zn concentrations in pore water were high (≤ 1.5 mg l^{-1}), biochar and biochar combined with greenwaste compost reduced these concentrations 10-fold for Cd, whilst Zn was also significantly reduced ($p < 0.05$). Greenwaste compost alone was not as effective, although concentrations were also significantly reduced and individual or combined application of amendments significantly reduced phytotoxicity (61% shoot emergence in untreated soil, 78% in amended soil; Beesley et al, 2010). In the case of As, concentrations in pore water showed a small increase with amendment application. At AE, biochar most effectively reduced pore water Cu concentrations (from > 1 mg l^{-1} in untreated soil to < 0.3 mg l^{-1} in amended soil), whilst greenwaste compost was more efficient for Pb (from > 70 mg l^{-1} in untreated soil to < 5 mg l^{-1} in amended soil). Uptake of Cu and Pb to ryegrass shoots decreased following amendment application, but biomass increased, especially in the combined biochar/compost amendment, due to large increases in available P and N (data not shown). Application of biochar alone resulted in lower DOC concentrations in pore water than greenwaste compost, compared to untreated soil (data not shown). Biochar alone was the only amendment not to significantly increase the harvestable amount of Cu, whereas greenwaste compost was the only amendment to significantly reduce harvestable Pb.

DISCUSSION

Biochar was highly effective at reducing Cd and Zn mobility, which would promote the establishment of cover on Cd and Zn contaminated soils by reducing phytotoxicity. In the case of As, the high pH of biochar (pH >8) could have impacted on this metalloid's mobility and explain why it was increased by biochar's application. For Cu, a positive correlation with DOC in pore water would explain why biochar reduced Cu furthest as DOC was increased only by the application of greenwaste compost and the combination of both amendments (data not shown).

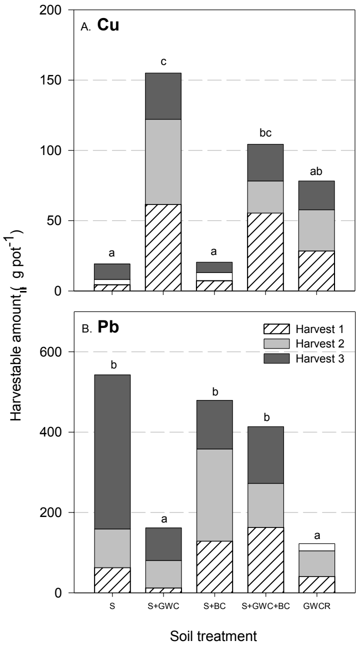

Fig. 1. Harvestable amounts of Cu (A.) and Pb (B.) in ryegrass (S = Untreated soil, S+GWC = soil plus green waste compost, S+BC = soil plus biochar, S+GWC+BC = soil plus green waste compost and biochar combined, and GWCR = green waste compost reference) Different letters indicate significant differences in total harvestable metal amounts between treatments ($p < 0.05$).

CONCLUSIONS

Biomass increases are desirable on degraded contaminated soils for stabilizing cover and reducing risk. However, the risk of pollutant transfer relates both to the uptake of metals and the biomass, on a cover area (harvestable) basis. Because of high biomass yields associated with greenwaste compost and compost and biochar, the reductions in ryegrass shoot metal concentration would not offset the risk of potential transfer of pollutants, so amendments needs careful and targeted application.

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REMEDIATION OF POPs POLLUTED SITES IN MOLDOVA

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ABSTRACT

The case studies on the remediation of POPs polluted sites in the Republic of Moldova are discussed in the article. The recommendations for further investigation of biotechnology for pollution site remediation was made with particular focus on .

INTRODUCTION

The inventory of obsolete pesticide storages in Moldova which was executed by Ministry of Environment and World Bank project revealed a large quantity of polluted sites (near 1590) which remain after the repacking and evacuation project [2]. Based on last inventory provided in fall of 2012 by the Ministry of Agriculture and Food Industry additional 150 tones of obsolete pesticides in 23 sites were discovered. The analysis has been made first of all for Persistent Organic Pollutants (POPs). More that 15 % sites were determined as extra high polluted territory with the POPs concentration in soil exceeding 50,0 mg/kg. The composition shows the presence of some of the world's most harmful chemicals including highly toxic pesticides such as HCH, DDT and industrial chemicals such as PCBs. The problem of residual content of old pesticides (OPs) in soil at former pesticide storages is acute for agricultural lands. POPs group is toxic, considered potential carcinogens and are listed as priority pollutants by the US EPA.

Some pilot projects were realized in Moldova for the assessment of different technology and remediation cost [1,3]. Three demonstration projects have been implemented to isolate the soil and building rubble in a controlled soil stockpile with impermeable top and bottom liners, covered by protective vegetation in clean topsoil: Bujor (Hincesti), Step-Sochi (Orhei) and Congaz (Comrat). The biotechnology demonstration was conducted at Bujor village by the soil cleaning with "Daramend" biological additives. The high risk from polluted territories was reduced by the application of the bioremediation and other environment-friendly technologies.
The phytoremediation technology was tested at another POPs polluted site (Balceana, Hincesti district). Several cultivated plants were evaluated for determination of pesticide extraction efficiency. The results of this experiment and review of previous studies showed a good extraction of DDTs, PCBs, and other chlororganic compounds from soil by zucchini and pumpkin plants [1. 4-7]. The design of a phytoremediation system varies according to the contaminants, the conditions at the site, the level of cleanup required and the plants used.
Currently were released products and universal biotechnological treatment of contaminated environments, such as bioremediation technologies "Daramend", "Terramend" production funding "Adventus Group", destined to eliminate POPs and hydrocarbon compounds for 70-250 days in soil and sediment [United Nations report, 2003]. However, as mentioned in the same report these biotechnologies are predestined remedy to low the medium concentrations of pollutants in soil and require adjustment to local pedological and microbiological conditions.

RESULTS OF SOIL REMEDIATION PROJECTS

Balceana site.

The determination of POPs concentration in soil samples in all case studies was made by gas chromatography method in accredited Moldavan laboratories (ISO17025). All territory surrounding the Balceana site is highly polluted by DDTs with concentrations more than 10 times the 100 μg/kg MAC. Two anomalous samples were identified with the unusually high pesticide concentrations greater than 50,000 μg/kg. Higher DDTs concentrations in soil were observed in the lower part of the site (fig. 1). The pollution level of HCHs is lower in comparison with DDTs. In the two anomalous samples high HCHs correlated with the DDTs results. The principal problem with this site is contamination by DDTs.

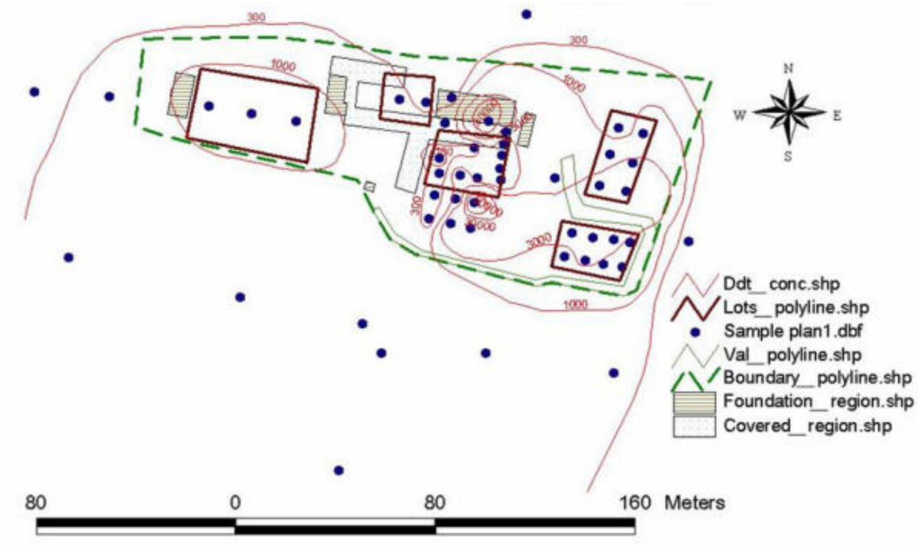

Fig. 1. Total DDTs concentration in surface soil of the Balceana site. Contours of equal concentration are given in µg/kg

Tab. 1. Estimated soil volume and mass with different concentrations of DDTs.

DDTs concentration, µg/kg	Area, m^2	Volume, m^3 to 0.5 m depth	Weight, tons to 0.5 m depth*
100 - 300	14982	7491	11986
300 - 1000	114320	57160	91456
1000 - 3000	16994	8497	13595
3000 - 10000	4857	2428	3885
10000 - 30000	1054	527	843
30000 - 50000	177	89	141
> 50000	52	26	41

The Bioaccumulation Factor (BAF), an important indicator of phytoremediation potential for POP polluted soil. Observed BAF values for all zucchini plants fluctuated from 0.5 to 4.0 for roots and from 0.3 to 4.3 for stems [1]. BAF greater than 1.0 shows evidence of accumulation potential since the concentration in plant tissue is greater than the concentration in soil. The BAF for roots and stems averaged over 1.0 with means of 1.90 and 1.64 respectively. BAFs for DDTs in plant tissues were very similar to observations for zucchini. The range of BAF for stem concentration varied from 0.45 – 3.01. The average decreased from 2.05 for roots to 0.82 for leaves. The weighted average value of BAF for zucchini was 1.10, and for pumpkin it was 1.42.

Bujor site

The contaminated construction waste and contaminated soil adjacent to the storage have been isolated in an on-site waste deposit with bottom and top protective liners (membrane), and secured by a surrounding protective bank and a top layer of clean soil. The total volume of waste amounted to 1,550 m^3. The remaining contaminated soil is treated by an *in-situ* bioremediation by land farming with addition of additives (nutrients, organic material as a microbiological carbon source, and reduced iron - The DARAMEND® process by ADVENTUS).

Sequential cycles of anaerobic (no oxygen, strongly reducing conditions) and aerobic (oxygen present) conditions enhance reductive dechlorination of chlorinated organics. The 10 cycles of treatment have been applied to the top soil at the demonstration site. The overall results after 10 cycles of treatment demonstrate appreciable reduction of soil concentrations of up to 84% for sum of DDT, 42% for sum of HCH and 76% for Heptachlor [3].

Tab. 2. Main concentration in treatment and control area before and after treatment with 10 cycles of Daramend

POPs concentration		Area 1	Area 2	Area 3	Area 4	Area 5	Control
Sum of HCH, mg/kg (%)	Initial	8.7	11.6	50.9	0.25	11.9	56.1
	5 cycles	5.1 (41%)	8.4 (28%)	26.0 (49%)	0.53	9.4 (21%)	65.3 (-)
	10 cycles	5.2 (40%)	14.0 (-)	25.0 (50%)	0.57	3.7 (68%)	9.2 (85%)
Sum of DDT, mg/kg (%)	Initial	35.9	10.5	12.9	0.57	22.8	1.5
	5 cycles	12.7 (65%)	2.2 (79%)	5.5 (57%)	1.3	13.5 (41%)	0.99 (34%)
	10 cycles	6.6 (82%)	0.48 (95%)	1.4 (89%)	0.22 (61%)	4.5 (80%)	0.99 (34%)
Heptachlor, mg/kg (%)	Initial	3.9	0.5	24.7	0.07	2.2	0.06
	5 cycles	0.49 (87%)	0.49 (2%)	4.6 (81%)	0.35	2.73	0.60
	10 cycles	2.3 (41%)	0.14 (72%)	4.5 (82%)	0.13	0.54 (75%)	0.04

CONCLUSIONS

Bioremediation has been shown to be an efficient and cost-effective treatment method for the cleanup of contaminated soils. As such, it has become one of the most promising technologies to consider in the remediation of contaminated sites in different countries.

Phytoremediation can be used for the remediation of polluted sites, however it needs to be designed based on local conditions. Investigators must take into consideration all advantages and limitations of this technology, considering such factors as plant selection, design of optimal plant density, and appropriate soil fertilization for the improvement of BAFs.

Bioremediation, including stimulating the native micro flora, bioaugmentation, phytoremediation and rizoremediation are the methods of cleaning soil contaminated with persistent organic pollutants that have already become common. The main technologies which are using microorganisms to decomposition in soil and water of pesticides, petroleum products, detergents include (i) creating conditions for activation of destructive capacity of native microflora (ii) introduction of microorganisms-destructors in soil or water (iii) use of appropriate bioreactors for the detoxification of highly polluted sites.

The next step of bioremediation technology development in the Republic of Moldova is suggestion to elaborate a complex approach by the utilization of the soil microbiology activation in the combination with phytoremediation and phytofixation. The microbiological strain, extracted from native soil microorganisms, will be used for the acceleration of OPs destruction. Such organisms are capable of breaking down organic contaminants to obtain food and energy, typically degrading them into simple organic compounds, carbon dioxide, water, salts, and other harmless substances.

The utilization of DARAMEND® technology in Moldavian conditions showed relative good results for OPs destruction. However the blank area without its application and where all procedures were made showed also the similar DDTs destruction. The hypothesis is that native microorganisms have possibility to destroy toxic substances where optimal conditions have been created.

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APPLICATION OF RISK ASSESSMENT PROCEDURE TO A REFINERY LOCATED IN A COASTAL SITE WITH NATIONAL INTEREST (ITALY)

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KEYWORDS
Contaminated sites, risk assessment, remediation

ABSTRACT

During last years, number of contaminates sites has increased more and more in Italy, because of accidental or voluntary pouring of pollutants into soils or into waters from industrial activities, or from uncontrolled deposits of urban and/or industrial waste, mostly toxic and harmful. Contaminated sites surely represent a risk for human health and for environment, thus they must be cleaned up.

Cleaning up environmental matrices and rescuing degraded areas are complex topics requiring specific technical and scientific competences, among which knowledge of suitable methodologies and tools in order to face problems emerging during the different phases of a remediation plan. One of these methodologies is represented by risk assessment (AdR), a large procedure which is nowadays largely adopted and applied at an International level in managing contaminated sites because it allows: to estimate risk for human health (inhabitants and workers) and for the environment which a contaminated site can produce at a quantitative way; to define limit concentration values for contaminated environmental matrices, corresponding with an acceptable risk and constrained by specific conditions of each site; to address remediation interventions to solutions which are compatible at an environmental viewpoint (not detaching from environmental conservation of system as a main element) and, at the same time, economically sustainable.

This paper reports application of risk assessment procedure (forward mode, according to M.D. 471/99) in the case of a refinery located in Italy, in one of the most known National Interest Sites. A good environmental characterization was basic in order to carry out site-specific risk assessment procedure, which led to remediation activities. GIS techniques were also used in order to support because they contain all necessary data and they also allow visualize different risk scenarios.

INTRODUCTION

Application of site-specific risk assessment procedure (AdR) was provided in Italy by M.D. 471/99. Nowadays, it is ruled by L.D. 152/06 and it is ended to identify threshold concentration values (CSR), which are considered as contamination levels for environmental matrices (saturated and unsaturated soil) whose exceed requires safety measures and remediation. According to the current procedure starting from concentration which is considered acceptable, we can estimate maximum tolerable concentration in correspondence of contamination source.

Application of AdR procedure is based on construction of a Site Conceptual Model (MCS). Defining MCS mainly consists in reconstructing characters of the three main AdR components:

Source => Transport => Target

About source, it is necessary to give a correct definition of its geometry, of its representative value as well as of its chemical, physical and toxicological features concerning each identified indicator pollutant. About transport, it is necessary to identify all possible migration ways by which contaminants can reach potential targets, estimation criteria of transport factors as well as criteria for determination of site-specific parameters which are useful for calculation of the transport factors themselves. About target components, all possible targets of contamination, both *on-site* and *off-site*, should be identified, as well as site-specific values to be ascribed to the corresponding exposure factors.

After defining MCS, current procedure (ruled by L.D. 152/06) is ended to estimate risk associated to a specific site and/or to carry out calculation of CSR for every identified secondary contamination source (soil, underground and groundwater). As a matter of fact, AdR may be applied by two modes: forward and backward. Forward mode was provided by M.D. 471/99 and it allowed estimate risk for health and environment associated to a contaminated site, starting from concentration observed at the source. Forward mode allowed verify acceptability of risk from residual concentrations, identified by BATs (Best Available Techniques).

AdR was applied by forward mode to a refinery located in one of the most interesting Sites with National Interest, both for social/environmental reasons and because of its representativeness, within a zone having strong industrial tradition on the coastal area of the Adriatic Sea. Inside the refinery area (surface 70 Ha), 128 tanks are present (storage over 1.500.000 m^3) and crude introduction wholly occurs through sea. Products are transported 30% through sea and 70% through land (five automated loading areas are there present). This refinery gives work to about 2,000 persons (among them, 500 are refinery workers) and has got a total processing capacity of more than 4,000,000 million tons of crude every year.

REMEDIATION PLAN AND RISK ASSESSMENT PROCEDURE

According to M.D. 471/99, some safety measures were carried out at the refinery area. In order to grant a complete obstacle for contaminated groundwater, a hydraulic barrier was there realized, formed by 26 extraction wells and 70 small wells for reimmission (realized along NE coastal border of the plant).

The remediation plan, as provided by M.D. 471/99, was divided into three main steps (Characterization Plan, Preliminary Project and Definitive Project) and included:

- geological and hydro-geological feature of the sites
- type of pollutants and the assumed migration model
- contamination confining, avoiding interferences with the environment and ensuring safety to workers by applying suitable emergency safety measures
- necessity of keeping the industrial activities in business
- need of adapting the interventions carried out in the past with the present remediation plan
- evaluation of costs and the estimation of the remediation times

Geographic Information Systems (GIS) have been very useful in the plan-draft and can also be applied to each of the single phases of remediation.

About geology of the area, unsaturated soil is almost everywhere characterized by layers formed by covering material, heterogeneous and mainly formed by sands and limy sands. It grows in thickness while moving towards the sea. Natural soils under covering materials are sands and gravels (mainly coarser material with a higher permeability than 10^{-3} m/s) along the bordering river; on the contrary, moving towards the opposite site, we can see more sandy and limy sandy soils with a medium permeability (about 10^{-4} m/s). West of railway line, we can find a bigger limy/clayey component, sometimes like lenses with a discrete thickness towards mounts. Considering lithology of natural soil at the site, along the river we could expect a better efficacy of remediation techniques based on convoying fluids into interstitial pores, on the contrary their application in the central and southern sides of the refinery was locally verified by tests. Further aspect limiting efficacy of techniques is presence of NAPL – non aqueous phase liquid - which must be firstly removed (Fig. 1), as it acts as a secondary contamination source. Tests were also adopted for other areas to be treated up the railway line, where presence of lenses of materials with low permeability embedded in coarser litho-types, could represent a limit for remediation efficacy.

Remediation plan concerning the refinery area was carried out by the following steps (according to M.D. 471/99):

1. Analysis of pollution included in the first step (Characterization Plan) and whose results were also basic in order to carry out site-specific risk assessment procedure.
2. Elaboration of a Conceptual Model (MSC, Fig. 2) supported by GIS systems, also basic in carrying out site-specific risk assessment procedure.
3. Study of possible application of remediation technologies (Preliminary Project).
4. Choice of the most suitable technologies, both for not constrained and for constrained areas and estimation of the achievable concentrations (Definitive Project).

1. Characterization Plan provided investigations in order to investigate concentration values in the environmental matrices. Soil investigation was carried out by percussion/direct push (Geoprobe R60) and included 2 points every 10,000 m^2, according to M.D. 471/99 (grid: 50 m meshes). By every survey, three samples were obtained: filling layer, soil, smear zone. Minimum depth of excavation was 4 m; maximum depth was down to 1 m deeper than the last contamination trace.

The aquifer level was identified by 53 piezometers at a variable depth between -1 and -3 m and it shows both daily (up to 50 cm) and seasonal (50-70 cm upstream; 70-120 cm towards the sea) variations. Conductivity of the aquifer litho-types ranges between $1.12*10^{-4}$ and $3.65*10^{-4}$ cm/s for coarser litho-types and between $3.76*10^{-8}$ and $4.46*10^{-9}$ cm/s for clay and loamy clay.

Thickness of recent deposit ranges between 25-30 and 40 m from the g.l. within the area of the river, where the substrate immersion seems NW.

Analysis of pollution aimed at finding out contaminants in the environmental matrices. In soil, both organic compounds (light and heavy HC, PAH at a punctual way, BTEX inside limited areas) and inorganic ones (Cd, Hg, Pb, Zn as mottled pollution) were found out. Exceed of law limits mainly interested soil thickness between -1.5 and -3.5 m. About groundwater, both organic compounds (BTEX, MTBE) and inorganic ones (Fe, Pb, Mn, Ni, Al, Se, Sb, As, Ag, Tl, sulfates, fluorides, nitrites, B) were found out. Exceeds were mainly concentrated at bordering areas, along the river and in the south-western side, on the contrary the middle area was about lacking.

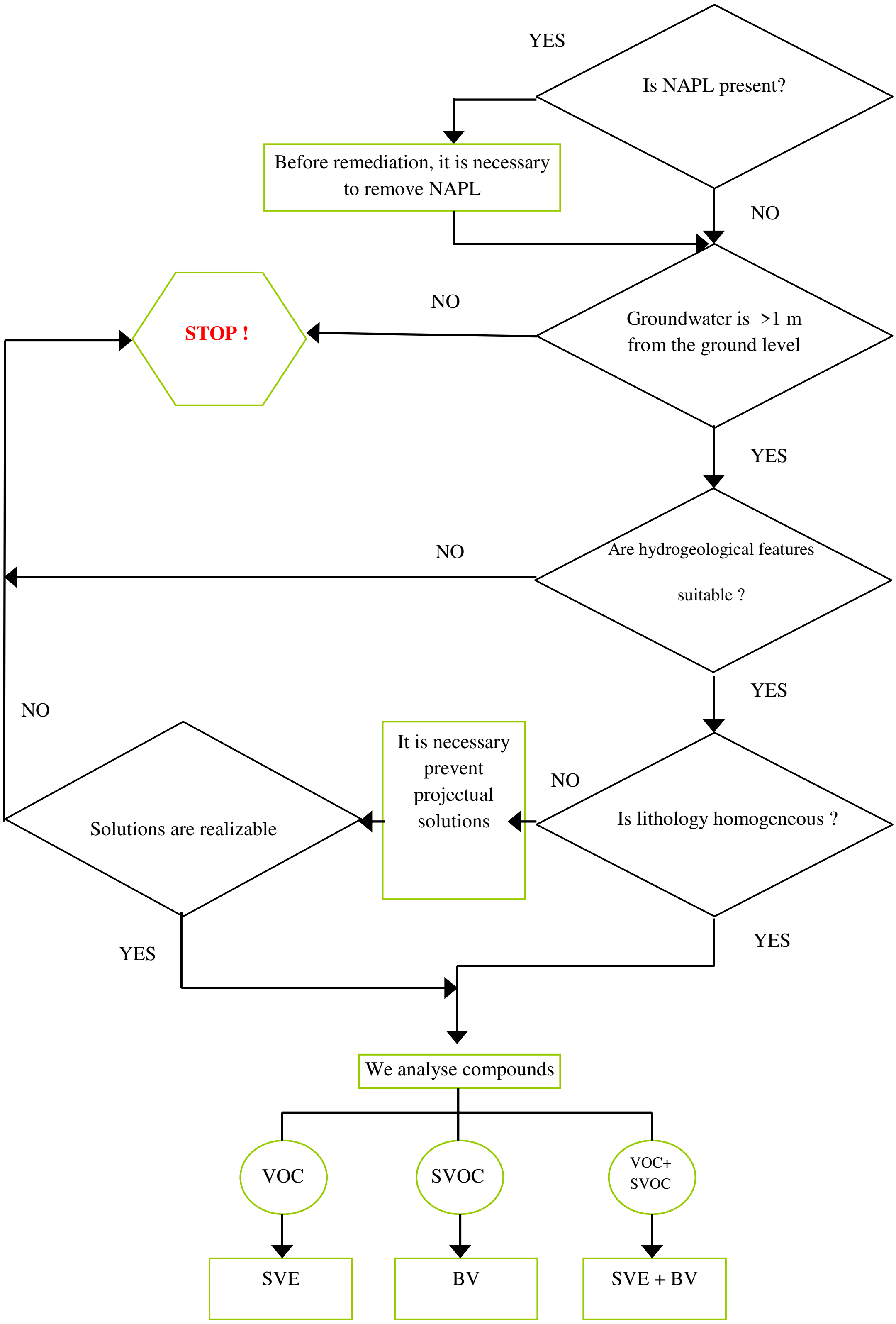

Fig. 1. Soil remediation. Choice of the most suitable technologies for not constrained areas. Criticities (such as the presence of thick lenses with a low permeability), similar for both treatments, can decrease the efficacy of treatments or increase their

duration; they can also force to use particular technical and projectual tricks but they don't prejudice their application. Lithology of the unsaturated soils to be treated is the main factor which influences their applicability and their efficacy.

In evaluating pollution from petroleum products, we couldn't consider every compound at a single way, obviously. Thus, besides controlling total data (often called TPH, Total Petroleum Hydro-carbons), we focused our attention on some chemicals of concern, chosen as representative of chemical, physical and toxicologic features of the several classes of compounds. Usually, mobility and toxicity of alcans, relatively low, make to move attention onto aromatic compounds and additives.
For lightest products (fuels), we generally consider BTEX, Pb additives and MTBE; for the heaviest ones, we move our attention onto PAH; medium products (kerosene, jet fuel) can have both BTEX and PAH.
About toxicity, Benzene is cancerogenic; some heavier PAH (i.e. benzo[a]pirene) are also suspected to be highly cancerogenic. Each of these groups has got its specific behavior in the soil.

2. MCS (Fig. 2) was realized within Characterization Plan and it was also basic in order to carry out risk assessment procedures.
MSC shows that contamination in dissolved phase can be ascribed, as far as HC compounds are concerned, to NAPL presence. The first end was thus maximizing and accelerating NAPL recovery by enhancing the existing recovery systems. In order to protect environmental targets, some emergence measures for NAPL removal were realized, and also a barrier in order to intercept GW at the sensible borders of the refinery. Wherever they found floating NAPL, they provided use of other immediate interventions: mobile bio-slurping systems, which allow removal of organic substances not only by mechanic recovery, but also by increasing their vaporization. From this viewpoint, some mobile skid systems seemed favorable because they could be located within areas where recovery operations make floating NAPL pockets more evident. NAPL recovery was carried out as a safety measure.

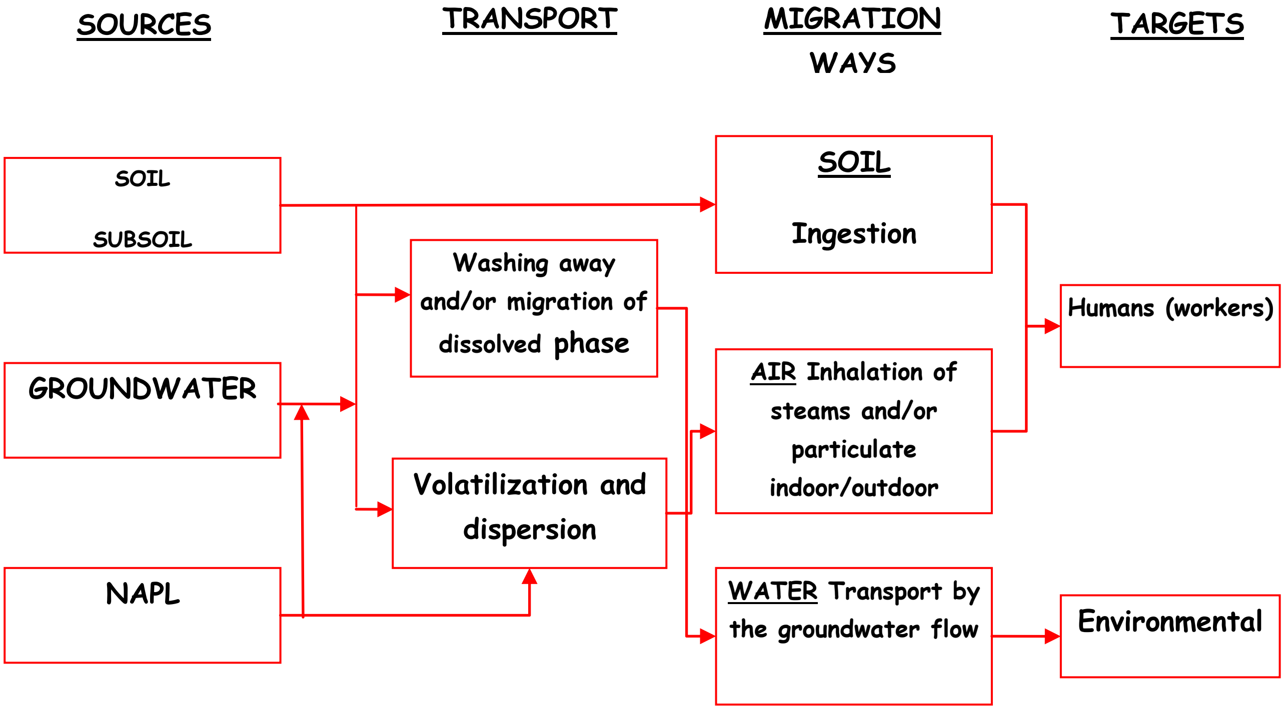

Fig. 2. MCS on which risk assessment procedure was based. *Source:* Preliminary Project.

3. The research of the most suitable technologies to be applied to this site concerned *in situ* treatments because:

a. working operations of the refinery must be ensured even during remediation
b. excavating inside the refinery could surely interfere with its structures and sub-structures
c. of the shallow GW level (–2m)

Whereas concentration limits provided by M.D. 471/99 show differences as far as maximum concentration limits in soils are concerned, distinguishing according to use destination of the site (residential or

commercial/industrial), concentration limits for groundwater were on the contrary unique: criteria in order to state such limits were ended to obtain drinking water. About it, it was obvious that till the site was still active, it shouldn't be possible to pump groundwater for drinking use, neither in correspondence of the site itself nor downstream. Because of it, it is obvious that remediation at this refinery in order to obtain concentrations below limits provided by M.D. 471/99 on the whole area while the site is still active should be hard at a technical way, because of limitations connected to use of such an area, and should be hardly kept in time because of possible further losses.
About the refinery, the following remediation ends were identified about groundwater (GW):

a. GW at the exit of the plant: lower concentrations than c.l. (M.D. 471/99, Att. 1). A big role was played by the hydraulic barrier projected and realized as an emergence measure, in order to contain pollution in a dissolved phase within the refinery borders and in order to stop transport of pollutants to the surface waters. Together with the TAF (Treatment of GW) plant, the barrier could also removed significant deals of GW pollutants.
b. Reduction of pollutants inside the plant till values that could guarantee an acceptable risk for workers (by carrying out a risk assessment procedure), because Preliminary Project showed the impossibility to reduce concentrations under limits provided by M.D. 471/99, Att. 1.

These ends were defined according to site constraints (pipelines, structures and sub-structures), which made hard to treat at some places, and according to refinery activity in progress, causing more pollution and suggesting remediation with safety measures.

4. The Definitive Project was elaborated at different ways for accessible areas and for constrained areas. Whereas in the first case, interventions concerning the smear saturated zones could be sized, in the second case a risk assessment had been necessary.
About not constrained areas, interventions for remediation of smear zone and saturated zone were sized. About groundwater, interventions on saturated zone allowed reduction in concentrations, even at dissolved phase. Because these areas were interested by contamination from VOC and SVOC, a sequence of technologies was carried out in order to remove firstly lightest compounds by volatilization (by using Air Sparging technology) and later on the heaviest ones by biodegradation (by using Bio-Sparging technology). In order to start treatment, a basic condition was removing NAPL both within the area itself and upstream. At any area, Soil Vapor Extraction (SVE) was also used as a safety measure in order to intercept compounds which the contaminated saturated area and the groundwater got free, besides being used as a remediation intervention on contaminated soil. In two of these areas, SVE had already been provided as a remediation intervention for unsaturated soil, thus its working was also protracted till the end of Air Sparging interventions.
Because of geological and hydro-geological conditions at the site, some measures were necessary in order to apply the above mentioned techniques, in particular, in order to apply SVE measures. As groundwater table is very shallow (about -2 m), and the most contaminated soils were in correspondence of the saturated zone, in order to keep dry the bottom of the excavation, it was thus necessary to adopt some systems able to lower groundwater level (such as some well point lines); it could avoid temporary interruption of SVE system applied as a safety measure in order to avoid steam formation underground.
Finally, Air Sparging allowed *in situ* volatilization and desorption of VOC by air bubbling through the contaminated aquifer and it was applied to homogeneous soils with high permeability. Bio-Sparging, applied after Air Sparging, works by accelerating action of the autochthonous bacteria by releasing air and nutrients.

About constrained areas, a risk assessment procedure had been necessary in order to realize whether risk could be considered acceptable or not. In the first case, remediation could be in fact carried out as soon as limitations on areas won't exist any longer, when plants are disposed. In case of not acceptable risk, on the contrary, some use limitations or protection measures should be necessary for human targets (refinery workers). Because the latter are only exposed to potential inhalation of contaminated steam, safety measures, besides consisting of DPI, should also consist in monitoring indoor or outdoor air quality.
A biodegradation was provided for four constrained areas, as it follows:

- anaerobic biodegradation by compounds with a slow Hydrogen release, only in the area which showed contamination by chlorinated compounds
- aerobic biodegradation by compounds with a slow Oxygen release, on the remaining areas.

Risk assessment had showed that there could be a risk for workers because of inhalation of indoor / outdoor steam. About environmental targets, the hydraulic barrier interrupts connections between sources and targets. Risk assessment had highlighted a not acceptable risk only for Benzene in correspondence with two piezometers even though the measured concentrations were much lower than TLV-TWA limits.

About soil, contamination by VOC and SVOC as well as specific features of the area (geological, hydro-geological and pollution) led to a serial application of two different remediation treatments (SVE and Bioventing). The shallow depth of the aquifer obliged to realize SVE not by vertical extraction wells, but by horizontal aspiration points located in suitable trenches, which gave higher costs and higher environmental impact as a result. Installing SVE required execution of a series of *in situ* preliminary tests, in order to determine the main parameters of the plan, in particular: air permeability tests for soil (in order to determine the influence ray of each single well) and a pumping test for groundwater (in order to determine transmissivity and storing coefficient of groundwater).

A risk assessment had been also realized in order to verify if measured concentrations in the soil during characterization (used as input concentrations) could remain at the site without being a risk for targets. The risk assessment had highlighted a not acceptable risk for inhalation of volatile compounds both indoor and outdoor. No risk had been instead revealed for direct contact in the 90% of the refinery area as risk is in this case connected with the absence of floor. The 10% of not paved area is not located within a critical area.

CONCLUSION

This study allowed confirm the validity of a multidisciplinary approach as a support to manage contaminated sites and, finally, to choose the most suitable remediation technologies to be applied.

This choice was carried out considering the geological and hydro-geological features, the type of pollutants and the assumed migration model, the contamination confining (avoiding interferences with the environment and ensuring safety to workers by applying suitable emergency safety measures), the necessity of keeping the industrial activities in business and of adapting the interventions carried out in the past with the present ones, the evaluation of the overall costs and the estimation of the remediation times.

The multidisciplinary elaboration that was followed in this specific case, concerning a refinery with structural and infra-structural constraints where working operations must be ensured during remediation, allowed us support the application of *in situ* treatments.

Risk assessment also played an important role within remediation plan of the studied refinery area. According to M.D. 471/99, site-specific risk assessment procedure was carried out after showing (by a Preliminary Project) that cleaning up by BATs couldn’t allow achievement of law limits at some areas.

About the mentioned risk connected with inhalation, for those areas whose risk revealed higher than the acceptable one, a periodical monitoring of some air micro-pollutants concentrations was planned according to the Law 626/94 about risk for chemical agents (TLV-TWA) for workers till the end of the refinery activities.

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ESTABLISH GEO-DATABASE ON ECOLOGICAL HEALTH OF THE MILITARY SITES IN MONGOLIA

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The main goal of the project is create a knowledge-base on ecological situation of former Soviet and current military sites in order to identify and further implement rehabilitation and restoration measures, thus recovering and sustaining an ecological function of the military sites to create suitable environment for further their use in civil society services in Mongolia. To achieve above-mentioned goal the following activities have been outlined in line with pre-defined objectives:

Objective 1. Introduce with the international practice on developing methodology of investigation and establishing Geo-database for identifying the ecological situation in/around military sites:

- Study tour of Mongolian specialists to Slovakia to introduce with methodology of conducting investigation in/around military sites and establishment of Geo-database,
- Literature review of research methods on investigating contamination by CBRN agents,
- Introduce with methods of laboratory analysis to identify level of contamination by CBRN agents.

Objective 2. Design and implement Geo-database on ecological status of military sites, especially those which are used by Soviet army during 1970–1990:

- Develop data list, logical design and physical design of Geo-database,
- Test Geo-database prototype,
- Data entry and quality assurance.

Objective 3. Diagnose and assess the level of contamination and degradation of military sites:

- Implement field training among specialists of Mongolian Army Force to conduct soil and water sampling, visual analysis of soil and water resources, and assess contamination rate,
- Collect soil and water samples from post Soviet and current military sites in accordance to the predefined sampling design,
- Conduct laboratory analysis for soil and water samples,
- Assess the level of contamination and land degradation in/around military sites,
- Develop map of the level of contamination and land degradation in/around military sites.

Objective 4. Develop scientific justifications for decontamination and rehabilitation of degraded military sites:

- Conduct study tour to introduce with innovative methods of decontamination of CBRN agents from soils and water,
- Develop Management plan from decontamination and rehabilitation of degraded military sites.

NATO PROGRAMME: **SCIENCE FOR PEACE AND SECURITY (SPS) PROGRAMME**

SPS KEY PRIORITY: Category A3a. Diagnosing the status of contamination by CBRN agents in military sites

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OTAN
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THE ACCUMULATION OF MACRONUTRIENTS BY MACROFUNGAL SPOROCARPS FREQUENT FROM VICINITY AN ALUMINIUM SMELTER

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KEYWORDS

Bioaccumulation, macrofungi, macronutrients, aluminium smelter

ABSTRACT

Environmental mineral macronutrients contents (P, K, Ca, Mg) in forest soil samples, in samples of fruiting bodies belong to dominant macrofungal taxa were analysed. Monitoring takes place at three research plots within beech-dominated forests localized near aluminium plant in Žiar nad Hronom (Central Slovakia, Europe). This research plots were in the last century more then 50 years long under different pollution load stress. The monitored macrofungi dispose of differentiated capability to accumulate macronutrients. In forest soils terrestrial saprotrophic species *Clitocybe nebularis* had effectively accumulate phosphorus, attaining the maximum of bioconcentration factor - BCF for mineral A-horizon (160.112 ± 69.651) and for organic soil horizons – O-horizons (10.556 ±1.381) too. Ectomycorrhizal species *Boletus chrysenteron* was rich on potassium in A-horizon (180.635 ± 33.474), also in O-horizons (18.843 ± 5.581).

Lignicolous saprotrophic species *Polyporus varius* accumulated calcium in comparison with A-horizon (9.358 ± 4.543), in a tiny extent with O-horizons (0.636 ± 0.315) and magnesium in comparison with A-horizon (14.152 ± 6.876) and with O-horizons (1.093 ± 0.283) too.

INTRODUCTION

One of the acute environmental problems today is depletion of soil macronutrients in forests. This excessive loss of macronutrients was observed in soils of forest ecosystems affected by long-term type of acidic air pollutants such as fly ash, hydrogen fluoride (HF), cryolite (Na_3AlF_6), aluminum oxide (Al_2O_3), sulfur dioxide (SO_2), carbon dioxide (CO_2), carbon monoxide (CO), tetrafluoromethane (CF_4) hexafluoroethane (C_2F_6) and polycyclic aromatic hydrocarbons (PAHs), which are emitted by the aluminum plant in Žiar nad Hronom mainly in the time period 1953 – 1996. Impact of air pollution on forest ecosystems, near Žiar nad Hronom previously evaluated Maňkovská & Steinnes (1995); Kuklová & Kukla (2008), Kozlov, Zverev, Zvereva (2009) and others. Fungi are involved in many processes affecting forest soil e.g. the aggregation and stabilization of soil structure, disintegration of various materials (e. g, rocks and minerals, plant debris, dead wood) and dissolution of soil minerals with fungal exudates. The notable importance of fungal activity in ecosystems endangered by air pollution lies in the ability of fungi to concentrate macronutrients in their biomass and to facilitate its return within the biogeochemical cycles back into the soil (Leake 2007, De Vries & Posch 2011). Mycelial fungal networks also playing a key role in the accumulation and mobilization of macronutrients and in their transport in soil (Gadd 2007). The accumulation of nutrients (P, K, Ca, Mg) were monitored in 2007 in the area of following monitoring sites (MP): MP Žiar, MP Močiar and MP EES. The greatest contribution to relative fungal abundance in the studied forest stands according to the authors Bučinová & Mihál (2008) shared lignicolous (wood-decaying) saprotrophic *Polyporus varius* (Pers.) Fr. *Xerula radicata* (Relhan) Dörfelt, with terrestrial saprotrophs *Gymnopus aquosus* Bull. Antonín & Noordel., *Clitocybe nebularis* (Batsch.) P. Kumm. and with ectomycorrhizal species *Boletus chrysenteron* Bull., *Russula foetens* (Pers) Pers. The aim of this work was assessing the bioaccumulation capability of selected fungal species.

MATERIAL AND METODS

Sites description

The monitoring sites are situated in the mildly warm climatic region, with the mean temperature in July 17-18 °C. The mean annual temperature is 6-7 °C, and the average annual precipitation reaches 700-800 mm (Lapin, 2002). Additional environmental characteristics of the monitored sites are summarized in the Tab. 1.

Representative samples of soil and surface humus horizons were sieved through a sieve with an aperture of 2 x 2 mm, dried at 80 ° C in a hot air dryer ABC GM 601.107 (ABC ELECTRO, France) and then homogenized with agate mill (Fritsch, Germany). Total elements content of calcium – Ca_t, potassium – K_t, magnesium – Mg_t, and phosphorus – P_t in soil samples was determined after microwave mineralization (Uni Clever – Plasmatronica, Poland) in hydrochloric acid and nitric acid solution by Inductively coupled plasma atomic emission spectroscopy (ICP-AES) method on device LECO ICP-3000 (Michigan, USA) according to the instructions given in Submanual for the sampling and analysis of soil on European Forest ecosystems - ICP Forests: [http://icp-forests.net/page/icp-forests-manual].

Tab. 1. Environmental characteristics of the samplig sites

Sites	Coordinates /Orografic unit/	Distance from the emission source /km/	Altitude /Meters above sea level/	Area $/m^{-2}/$	Forest stand age /Years/	Soil types/ Humus types	Plant cover /%/	Forest types Herbs cover /%/
MP Žiar	48º32`38``N 18º51`43``E / Štiavnické vrchy Mts./	1.5	470	1600	90	+ Stagni-Dystric Cambisols/ moder	5	+*Fagetum pauper*: *D.bulbifera* (+ – 10%) *D.f.mas* (5 – 10%)
MP Močiar	48º33`98``N. 18º56`93``E / Štiavnické vrchy Mts./	7	610	2500	100	+ Dystric Cambisols/ acidic mull	25	+ *Fagetum pauper*: *C.pilosa* (0 – 5%) *D.bulbifera* (5 – 10%)
EES	48º38`10``N 19º04`08``E /Kremnické vrchy Mts./	18	460 -510	1500	110	* Cambi-Dystric Andosols/ acidic mull	50	* *Fagetum pauper*: *C.pilosa* (+ – 20%) *D.bulbifera* (1 – 5%)

*after Kuklová et al. (2005); + Sýkora 2009

Dominant species samples of *P. varius, X. radicata, G. aquosus, C. nebularis, B. chrysenteron, R. foetens* were dried at 80 ° C in a hot air dryer ABC GM 601.107 (ABC ELECTRO, France), homogenized with agate mill (Fritsch, Germany) and mineralized via microwave mineralization (Uni Clever – Plasmatronica, Poland) in hydrochloric acid and nitric acid solution by Inductively coupled plasma atomic emission spectroscopy (ICP-AES) method on device LECO ICP-3000 (Michigan, USA) according to the instructions given in Submanual for the sampling and analysis of soil on European Forest ecosystems - ICP Forests: [http://icp-forests.net/page/icp-forests-manual] to determine total elements (Ca_t, K_t, Mg_t, P_t) in macrofungal sporocarps. The bioconcentration factors (BCF) for studied macrofungi were calculated as ratio:

BCF = macronutrient concentration in macrofungal sporocarps:macronutrient concentration in soil (separately for A-horizon and for Organic horizon).

RESULTS AND DISSCUSION

All surveyed macronutrients were recorded in the surface humus horizons in greater mass, then in the organo-mineral soil A- horizons. Bioconcentration factors of sporocarps to A- horizons were much higher than bioconcentration factors of sporocarps to O-horizons. *Clitocybe nebularis* can efficient accumulate phosphorus (Fig. 1) and bioaccumulation of its sporocarps from surface humus horizons provides lower values (mean 10.556 ± 1.381) then bioaccumulation from soil (mean 160.112 ± 69.651). Kalač (2009) reported that fungi are able to accumulate phosphorus in 10-50 fold concentration compared to its content in the substrate and the best accumulators are saprotrophic terrestrial species. *Boletus chrysenteron* show higher potassium bioaccumulation (Fig. 2) from soil (mean 180.635 ± 33.474) then from surface humus horizons (mean 18.843 ± 5.581), what correspond with the ability of macrofungal fruiting bodies accumulate 20 to 40 times the amount of potassium present in the substrate Kalač (2009).

Bioconcentration factors of calcium (Fig. 3) for *Polyporus varius* provides lower values (mean 0.636 ± 0.315) in surface humus horizons compared to bioconcentration factors of sporocarps to soil (mean 9.358 ± 4.543). Bioconcentration factors of magnesium (Fig. 4) *Polyporus varius* sporocarps to soil (mean 14,152 ± 6.876 were lower then bioaccumulation factor of sporocarps to surface humus horizons (mean 1.093 ± 0.283) too. After Seger & Hüttner (1981) macrofungi accumulate calcium and magnesium from substrates only insufficiently, except lignicolous saprotrophic family Polyporaceae.

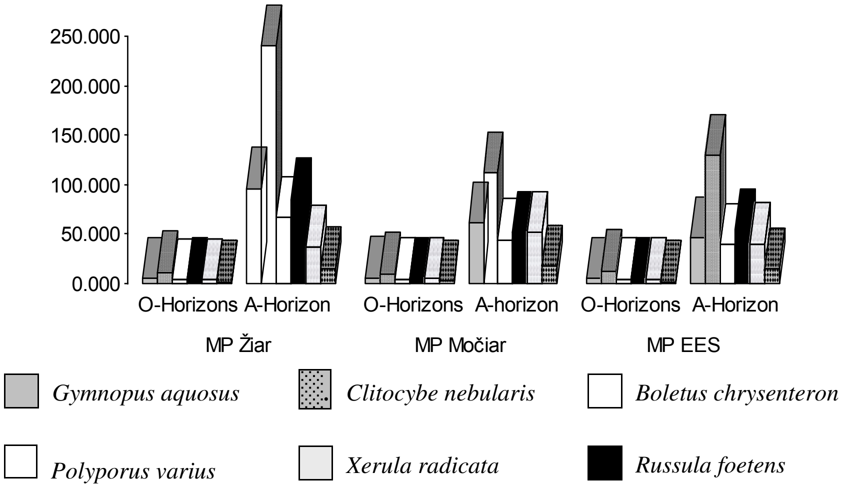

Fig. 1. The bioconcentration factors of phosphorus (P), in sporocarps of selected macrofungi

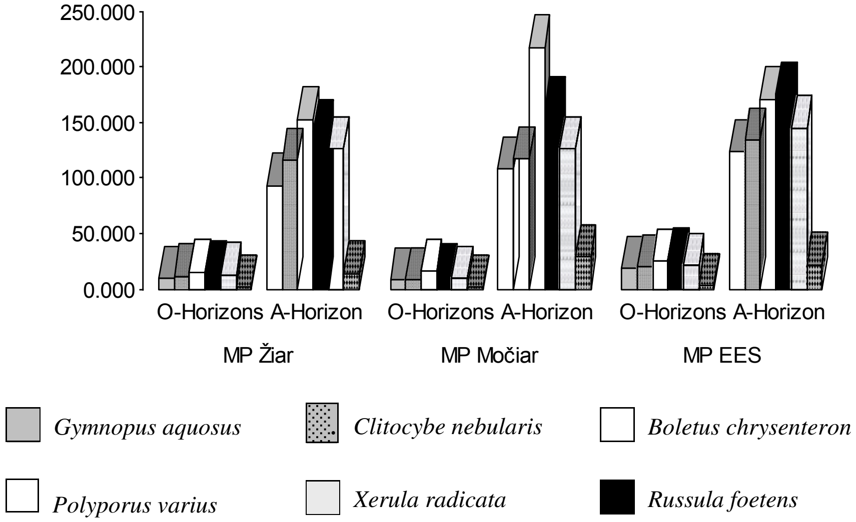

Fig. 2. The bioconcentration factors of potassium (K), in sporocarps of selected macrofungi

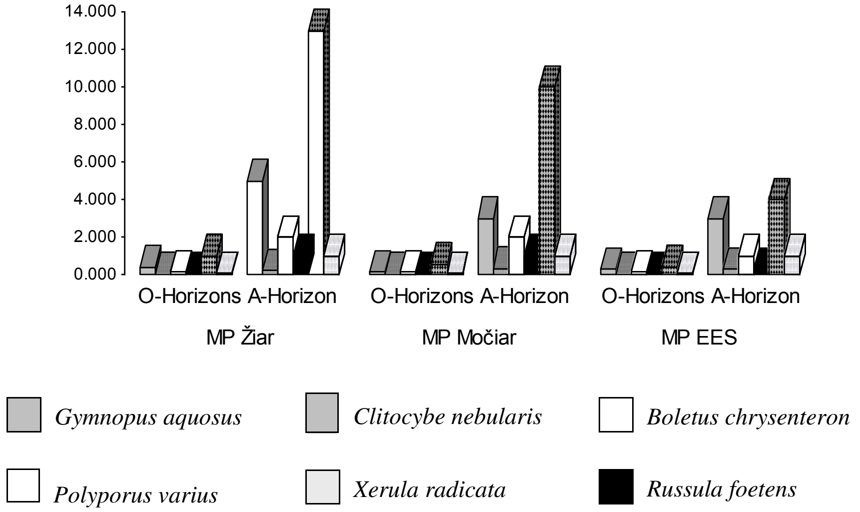

Fig. 3. The bioconcentration factors of calcium (Ca), in sporocarps of selected macrofungi

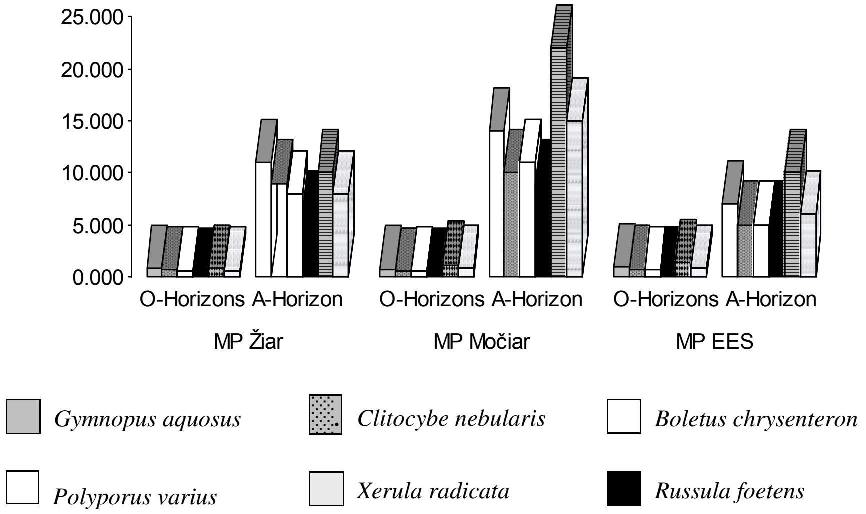

Fig. 4. The bioconcentration factors of calcium (Ca), in sporocarps of selected macrofungi

CONCLUSIONS

Terrestrial saprotrophic species *Clitocybe nebularis* had effectively accumulate phosphorus and ectomycorrhizal species *Boletus chrysenteron* potassium. *Polyporus varius* can only slightly accumulate both macronutrients calcium and magnesium.

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EVALUATION OF BIODEGRADATION DURING THE VAPOR INTRUSION OF PETROLEUM HYDROCARBONS

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KEYWORDS

Contaminated Sites, Vapor Intrusion, Petroleum Hydrocarbons, Natural Attenuation

ABSTRACT

Natural Attenuation can significantly influence the potential impact of petroleum hydrocarbon spills, by reducing, mainly through biodegradation processes, the mass, mobility and concentration of contaminants. These processes can be particularly effective in attenuating petroleum hydrocarbon vapors, either from groundwater or unsaturated soil sources. Nevertheless, most risk assessment procedures do not include vapor degradation as a standard feature for developing clean-up levels (e.g. the Johnson and Ettinger model). Neglecting these processes can lead to an overestimation of the overall risk for human health, since vapor intrusion in indoor air is one of the most important exposure pathways at many contaminated sites impacted by volatile compounds. Hence the present work aims to identify, using a model that includes anaerobic and aerobic biodegradation, under which site conditions biodegradation is expected to play a significant role in attenuating degradable vapors migrating from source to enclosed spaces.

INTRODUCTION

Vapor intrusion in indoor environments is one of the most important exposure pathways at many contaminated sites impacted by volatile compounds (Hers et al. 2003). Consequently the significance of this pathway is the subject of intense debate (Johnson et al. 1998) and in the last years this issue has been the focus of a number of studies (see references). Actually this topic has been addressed since the 1980s, initially with the emphasis placed on assessing impacts of naturally occurring radon intrusion. In 1991 a model for screening-level calculations (Johnson & Ettinger 1991) was developed. Such a model, which is still now the most widely used algorithm for the vapor intrusion pathway, incorporates both convective and diffusive mechanism for estimating the transport of contaminant vapors from soil or groundwater into indoor space. However several field investigations have shown that the J&E model often over-predicts the indoor concentration of contaminants at sites impacted by petroleum hydrocarbon compounds (Johnson, 2002; Provoost et al., 2007). This is especially related to the fact that the J&E algorithm does not include biodegradation, which the field studies have shown to be particularly effective in attenuating vapors (Roggemans et al., 2001; Fischer et al., 1996; Luo et al., 2009; Lahvis et al., 1999; McAlary et al., 2007; Lundegard et al., 2008).

A range of numerical (e.g. Abreu et al., 2009; Hers et al., 2000; Bozkurt et al., 2009; Yu et al., 2009) and analytical (e.g. Johnson et al., 1998; DeVaull, 2007; Davis et al., 2009; Parker, 2003; McHugh et al., 2006; Verginelli et al., 2010; Mills et al., 2007) models including aerobic biodegradation were developed to overcome this limitation. These models differ by the underlying assumptions and the conditions at which they can be applied. For instance, some models describe the transient behavior of the vapor intrusion process (e.g. Mills et al., 2007; McHugh et al., 2006), other the spatial variability (Abreu et al., 2009), the non-homogeneous soil conditions (Bozkurt et al., 2009), the oxygen-limited biodegradation (e.g. DeVaull, 2007; Verginelli et al., 2010) or the volatilization from soil contaminated by NAPL (Parker, 2003). All these models account just for the aerobic reaction; whereas, anaerobic biodegradation is always neglected. However, as reported by Foght (2008) and Haeseler et al. (2010), in the last decades several studies have demonstrated that many aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene (BTEX) and some polycyclic aromatic hydrocarbons (PAHs) can be completely degraded under anaerobic conditions. In fact these experimental and field studies have shown that, under oxygen deficiency, anaerobic bacteria can use nitrate, sulfate, iron, manganese and carbon dioxide as their electron acceptors and break down organic chemicals into smaller compounds even though with usually much slower rates than the aerobic reaction (Schreiber et al., 2004).

Besides, anaerobic biodegradation can potentially take place near the vapor source zone where the oxygen concentration may result below the minimum level required to sustain aerobic biodegradation (Boopathy, 2004; Dou et al., 2008; Lee et al., 2001; Johnson et al., 2006; Molins et al., 2010; Bekins et al., 2005; Gray et al., 2010; Salminen et al., 2004). This is somehow confirmed by the frequent methane detection at sites where petroleum hydrocarbons have been released into the subsurface (e.g. Lundegard et al., 2006; Lundegard et al., 2008; Hers et al., 2000; McAlary et al., 2007), suggestive of anaerobic biotransformation under methanogenic conditions (Bekins et al., 2005; Gray et al., 2010).

To assess how aerobic and anaerobic biodegradation might influence the attenuation of vapors in the sub-soil, in this paper a steady-state analytical solution of a 1-D vapor intrusion model including both aerobic and anaerobic biodegradation was used (Verginelli and Baciocchi, 2011).

MODEL DESCRIPTION

The reactive transport of VOC vapors and oxygen has been described by two coupled diffusion-convection differential equations with reaction terms at steady-state:

$$\begin{cases} D_v^{eff}\dfrac{d^2C_v}{dx^2} - v_D \cdot \dfrac{dC_v}{dx} - R_v(C_v, C_{O_2}) = 0 \\ D_{O_2}^{eff}\dfrac{d^2C_{O_2}}{dx^2} - v_D \cdot \dfrac{dC_{O_2}}{dx} - R_{O_2}(C_v, C_{O_2}) = 0 \end{cases}$$

Where the subscripts v and O_2 refer to the vapor phase contaminant and to oxygen, respectively. C is the concentrations of the species in the soil-gas phase, R the reaction rates, v_D the Darcy velocity and D^{eff} the effective porous medium diffusion coefficients.

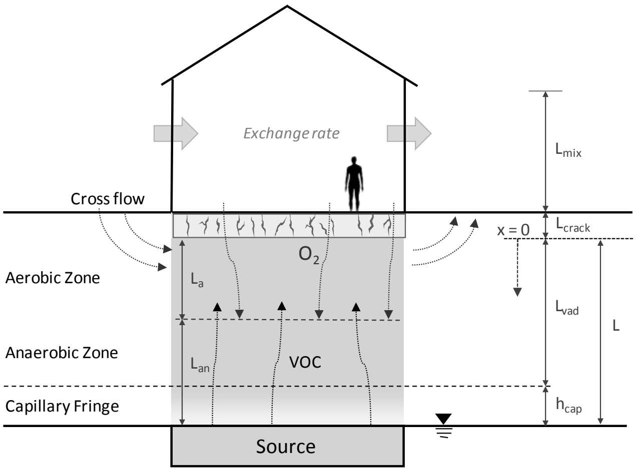

Fig. 1. Conceptual Model. The symbol x represents the spatial variable and is positive with increasing depth. The origin of x is at the bottom of the building.

The reaction rates R in the soil matrix were assumed to be first-order in C_v:

$$R_v(C_v, C_{O_2}) = \begin{cases} \alpha_a \cdot C_v & for \quad C_{O_2} \geq C_{O_2,tresh} \\ \alpha_{an} \cdot C_v & for \quad C_{O_2} < C_{O_2,tresh} \end{cases} \quad ; \quad R_{O_2}(C_v, C_{O_2}) = \begin{cases} \gamma \cdot R_v(C_v, C_{O2}) & for \quad C_{O_2} \geq C_{O_2,tresh} \\ 0 & for \quad C_{O_2} < C_{O_2,tresh} \end{cases}$$

Where $C_{O2,tresh}$ represents the oxygen threshold concentration required to sustain aerobic biodegradation. Some studies suggest that aerobic biodegradation of hydrocarbons stops, or slows down to very low rates, when oxygen soil gas concentration falls below approximately 2% v/v (Roggemans et al., 2001).

In the case of aerobic biodegradation, the oxygen reaction term, R_{O2}, is related to R_v by the stoichiometric mass ratio (γ) between oxygen and the compound(s) of concern.

Since biodegradation is commonly assumed to take place in the water phase of the unsaturated soil porosity, the kinetic rate constants for the aerobic or the anaerobic reaction, α_i, can be expressed, assuming linear equilibrium partitioning, as follows:

$$\alpha_i = \frac{\lambda_i \cdot \theta_w}{H}$$

where the subscript i refers either to aerobic (a) or to anaerobic (an) biodegradation, respectively. λ is the intrinsic degradation rate constant, θ_w the water-filled porosity of the soil and H the Henry's law constant.

To solve the two coupled differential equations, the whole domain was divided into regions characterized by different behaviors (see Fig. 1). For each region the differential equations were separately integrated by imposing the boundary conditions at the interfaces, allowing to obtain the expressions for the vapor phase concentration and flux profile along each zone. Next, the expressions for the unknowns needed to solve the equations were derived by equating the fluxes at the interface between the contiguous layers. The expressions obtained are reported in the following.

Concentration at the aerobic to anaerobic interface. The concentration C_a at the aerobic to anaerobic interface ($x = La$) was obtained by imposing the continuity of the two fluxes at the interface:

$$C_a = \frac{C_{source,sg}}{\cosh\left(k_{an} \cdot L_{an}\right) + \left(\frac{k_a \cdot D_a}{\tanh(k_a \cdot L_a)} - \frac{k_a \cdot D_a}{\alpha_R \cdot \sinh(k_a \cdot L_a)}\right) \cdot \frac{sinh\left(k_{an} \cdot L_{an}\right)}{k_{an} \cdot D_{an}}}$$

With:

$$\alpha_R = \cosh(k_a L_a) + \frac{\sinh(k_a L_a)}{k_a \cdot D_a \cdot \left(R_{crack} + R_{mix}\right)}$$

L_a and L_{an} are the aerobic and anaerobic layer thickness, respectively. k_a and k_{an} are parameters which give an indication of biodegradation relevance relative to diffusion, in terms of the inverse of the diffusive-reaction length:

$$k_i = \left(\frac{\lambda_i \cdot \theta_w}{H \cdot D_i}\right)^{1/2}$$

The subscript *i* refers to aerobic (*a*) and anaerobic (*an*) biodegradation respectively.
R_{mix} represents the dilution factor due to air building exchange (*ER*):

$$R_{mix} = \frac{1}{L_{mix} \cdot ER}$$

Where L_{mix} is the enclosed space volume/infiltration area ratio.
R_{crack} represents the attenuation contribution of cracks:

$$\begin{cases} R_{crack} = \left(R_{mix} + \bar{i}\frac{A_b}{Q_s}\right) \cdot \left(\exp(\bar{i} \cdot \xi) - 1\right) & (\Delta p \neq 0) \\ R_{crack} = \dfrac{L_{crack}}{D_{crack}^{eff} \cdot \eta} & (\Delta p = 0) \end{cases}$$

With:

$$\xi = \frac{Q_s}{A_b} \cdot \frac{L_{crack}}{D_{crack}^{eff} \cdot \eta}$$

L_{crack} is the foundation thickness, A_b the foundation area in contact with soil, η the foundation crack fraction, Q_s the convective flow rate from the soil into the building and *i* the unit vector of the convective flow depending on the pressure difference (Δp) between the soil and the building and is equal to i=1 in the case of positive building pressure (i.e. $\Delta p > 0$) and to i = -1 for negative building pressure ($\Delta p < 0$).

Concentration at the bottom of the basement.The concentration, C_0, at the bottom of the basement ($x = 0$) was obtained imposing the continuity of the two fluxes at the interface:

$$C_0 = \frac{C_a}{\alpha_R}$$

Indoor Concentration . Finally using the expression derived for the flow through the foundations and accounting for the vapors dilution due to building air exchange rate, the indoor concentration, C_{indoor}, can be calculated as:

$$C_{indoor} = C_0 \cdot \frac{R_{mix}}{R_{crack} + R_{mix}}$$

RESULTS AND DISCUSSION

The model was used to assess under which site conditions biodegradation is expected to play a significant role in attenuating degradable vapors migrating from source to enclosed spaces and to evaluate the contribution of the aerobic and anaerobic attenuation pathways. To this end, solutions have been calculated, using representative parameter ranges and values. The foundation crack fraction, η, was set equal to 0.0001, that is much lower than the ASTM (2000) standard value (η = 0.01). The choice of this value is in line with the results based on measurements of air-entry rates for radon, which provided a range between 0.001 and 0.0001 (e.g. Nazaroff, 1992; Revzan et al., 1991). The convective flow rate, Qs, was set equal to 3 L/min which is representative of the range suggested by Hers et al. (2003). The aerobic and anaerobic biodegradation rate constants used as reference value in this work are the geometric mean, obtained through a detailed statistical analysis of several field and laboratory studies, by DeVaull (2007) and Aronson and Howard (1997) respectively.

Fig. 2 reports an example of the predicted different behavior, in terms of the toluene attenuation factor (calculated considering both aerobic and methanogenic anaerobic biodegradation) as a function of the source concentration, assuming a soil contaminated by toluene only (Fig.2a), by a BTEX mixture (Fig.2b), by Fresh Gasoline (Fig.2c) and by Weathered Gasoline (Fig.2d).

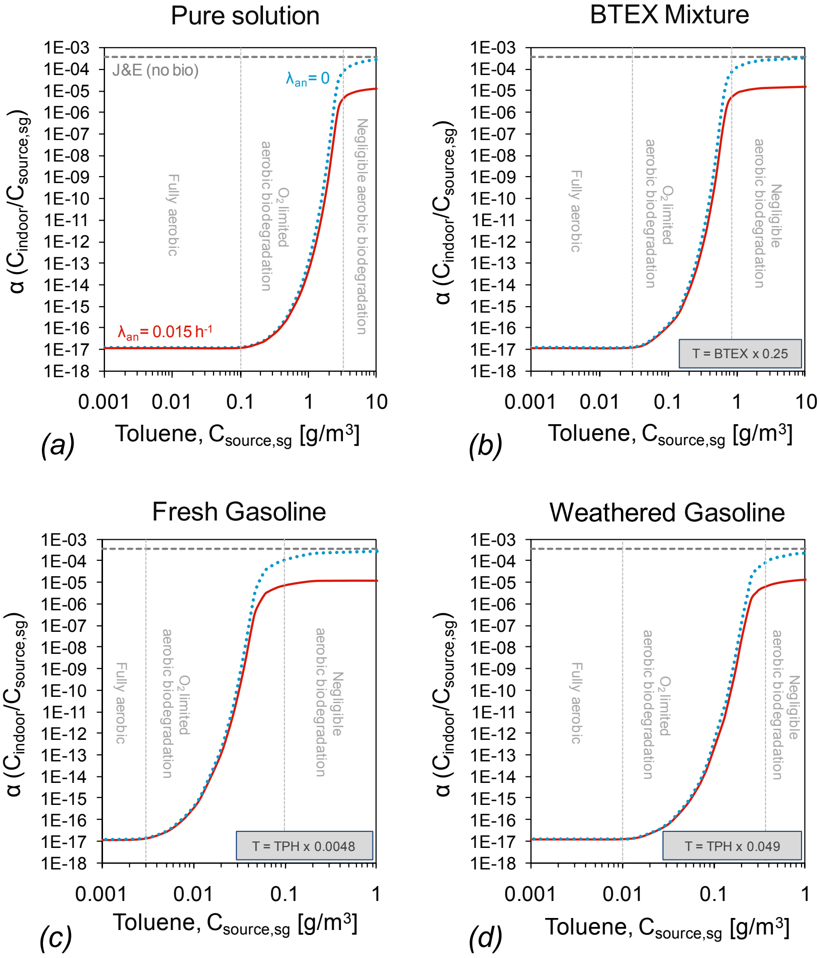

Fig. 2. Predicted toluene attenuation factor vs. toluene soil-gas source concentration in the case of a soil contaminated by (a) Toluene, (b) BTEX, (c) Fresh Gasoline and (d) Weathered Gasoline source. Aerobic and methanogenic anaerobic biodegradation (continuous line); Aerobic and negligible anaerobic reaction (dashed lines). For reference the results obtained by the Johnson & Ettinger model also reported.

As expected, the results obtained show that the predicted toluene attenuation factor, calculated at the same toluene source concentration, is typically higher when toluene is present as one of the components of a hydrocarbon mixture, either it is a BTEX mix or a gasoline one. Such a behavior is particularly relevant for intermediate to high source concentrations. Namely, in this specific case, an increase of the attenuation factor, in the case of toluene only, is observed for toluene concentration ($C_{source,sg}$) above 0.1 g/m^3, whereas for a Fresh Gasoline source this conditions is reached for $C_{source,sg}$ > 0.003 g/m^3. Indeed, the presence of a mixture of hydrocarbons increases the oxygen demand and thereby reduces the thickness of the layer where aerobic biodegradation occurs. Furthermore, in this case (i.e. methanogenic anaerobic biodegradation) the presence of a mixture causes an increase of methane production which, as described above, leads to an higher oxygen consumption in the aerobic zone with a consequent further reduction of the aerobic biodegradation pathway.

CONCLUSIONS

The model described in this paper was applied to assess the combined effects of aerobic and anaerobic biodegradation on the overall attenuation of vapors migrating into indoor environments. The obtained results suggest that for many scenarios, the aerobic biodegradation is expected to be the main attenuation mechanism. This is due to the fact that the kinetic rates for aerobic biodegradation are generally much faster than anaerobic processes (up to two orders of magnitude). However, in cases where the aerobic biodegradation is limited by the oxygen availability (e.g. for high source concentrations) anaerobic biodegradation may lead to a significant further attenuation. Such attenuation is very relevant especially when anaerobic biodegradation occurs under denitrifying or sulfate reducing conditions only (i.e. no methane generation). However, as shown by several field studies, this condition is uncommon since methane, suggestive of the occurrence of anaerobic biotransformation under methanogenic conditions, is frequently detected at sites where hydrocarbons have been released. In this case the generation of methane leads to an increase in oxygen consumption, due to oxidation, with a reduction of the aerobic layer thickness and consequently of the overall attenuation. Nevertheless, even in the presence of methane production, the occurrence of anaerobic biodegradation can lead, especially for high source concentrations, to a significant further attenuation.

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THE IMPORTANCE OF THE INVOLVEMENT OF STAKEHOLDERS IN STEERING COMMITTEES OF THE NATIONAL CONTAMINATED SITES INVENTORY PROJECT (NIKM)

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KEYWORDS

Contaminated sites, inventory, steering committee, project board, project management, PRINCE2

ABSTRACT

The preparatory - 1st stage of the project - National Inventory of Contaminated Sites (NIKM) in the Czech Republic is nearly finished. NIKM, the project co-financed from the Operational Programme for the Environment should continue into its 2nd stage, the start of which is slightly postponed.

The main result from the 1st stage was the approved methodology of the inventory and a draft project of the following – the 2nd stage of NIKM. This includes a proposal for a new structure of the steering committees. From this structure the participation of stakeholders external to the Ministry of Environment is excluded. Having in mind a set of expected project outcomes – inventory for the whole country's territory, but edited in the 14 regional reports – it is logically important to have also some feedback from future users – from regional offices and other institutions and bodies of the public administration. During the course of the project, the experience and expertise of stakeholders' representatives can be used for the ongoing review of phase outcomes and for the supervision of the project.

INTRODUCTION

The first stage of the NIKM project [1] [2] was conducted during the period 2009 – 2013, as a project of the Operational Programme of the Environment 2007-2013, Priority axis 4 - The Improvement of Waste Management and the Rehabilitation of Old Environmental Burdens, the Area of intervention 4.2. - The Rehabilitation of Old Environmental Burdens. From 2013 it should be followed by the second (implementation) stage. In the 1st stage the project team created and verified methodology for the nationwide inventory. The project included the extraction and consolidation of the existing information on contaminated sites, involvement of remote sensing in identifying potential contaminated sites, design of inventory tools and practices and the development of the knowledge base for the nationwide inventory. The methodology was successfully verified in 9 % of the territory of the Czech Republic. On the basis of the methodology a procedure for the nationwide inventory, including time scheduling and financial costs, was drafted.

The authors of the contribution participated in the project steering committees' structure (M. Blahutová as a member of the Monitoring Committee on behalf of the Ministry of Industry and Trade and Z. Suchánek as a Project Lead and a member at all levels of the project board).
Based on the experience from the activities at all levels and the forms of the steering committees ("project board") in the 1st stage of NIKM, we would very much appreciate an involvement of future users (stakeholders) in the so called Monitoring Committee and to argue for also continuing this approach during the implementation stage of NIKM.

Steering bodies of the 1st stage of NIKM

The draft project of the 1st stage of NIKM [1] designed several types/levels of steering bodies. The hierarchical structure started with the Monitoring Committee (created by the Ministry of the Environment – MoE - in its role as the responsible body for tasking the theme for the Operational Programme of the Environment in view of the needs and fulfilling of the State Environmental policy), then continuing with the Coordination Committee (responsibility of the MoE, participation of State Environmental Fund - SEF / Operational Programme Environment – OPE, and CENIA as the project executive organization) and the Realization Committee (CENIA and suppliers, MoE and SEF/OPE only as observers). All these bodies have their Statutes and Rules of procedures. The frequency of individual meetings is provided in table 1. It can be concluded that 54 meetings satisfactorily assured the regular and smooth performance of the project. There were less ad-hoc meetings than planned, because their role was overtaken by more frequent brainstorming seminars (usually 2 day events out of the office, with the participation of coordination and realization committees' members). Protocols (minutes) from those events were very detailed (65 pages in total – see table 1) and served as basic documents for change management. The number of "Inspection days" was less than planned, because of the checking of activities and because of the fulfilment of tasks, which was a routine part of each Coordination Committee meeting.

Tab. 1. Forms of the 1st stage of the NIKM project steering bodies and the statistics of their meetings

1st stage of NIKM project [1]		**No. of meetings -planned/performed**						
		2008-2009	**2010**	**2011**	**2012**	**2013**	**2009-2013**	**Σ**
Monitoring committee		2	2	2	1	0	7	54
Coordination committee + Inspection day/ expanded inspection day	Coordination committee	4	3	3	3	(1) 1)	14	
	Inspection day	2/0	3/1	3/3	2/2	1/0	11/6	
Realization committee		2	2	5	4	(1) 1)	14	
Ad hoc meetings: Operational coordination meeting/Consultation meeting		5/2	3/0	2/1	2/0	2/0	14/3	
Brainstorming seminar (workshop)	No. of seminars	1/0	1/2	1/7	1/1	1/0	5/10	
	No. of minutes pages	0	14	44	7	0	65	

Note: 1) presumed

Monitoring committee

The Monitoring Committee had a special role to play, 7 sessions which were usually in the form of a seminar or conference. This body was very important namely in the obtaining of feedback from a part of future project outputs – from representatives of 14 regions, Ministries (of Interior, Industry and Trade, Agriculture) and specialized institutions. The Monitoring Committee has up to 40 members.

Steering bodies of the 2nd stage of NIKM

A proposed structure of steering committees for the 2nd stage of NIKM and expected outcomes of the 2nd stage are described in draft project [3] [4]. This proposal respected a draft guideline of the Ministry of the Environment regarding steering bodies of the ICT projects (2011). The structure of MoE steering bodies for these types of projects is still under development. In table 2 we provide a comparison of the Steering Bodies' structures for the 1st and the 2nd NIKM stages and the PRINCE2 principles [5].

PRINCE 2

The project management methodology PRINCE2 (an acronym for **pr**ojects **in** **c**ontrolled **e**nvironments, version **2**) is generally recommended as a management standard not only for IT projects but for all public projects. This is typical in the NIKM project's case.

PRINCE2 is a process-driven project management method developed by a UK government agency. It comprises the management, control and organisation of a project. We seek inspiration in defined roles and responsibilities, which appear in Annex C of the PRINCE2 2009 edition (Project Board; Executive; Senior user; Senior supplier; Project manager; Team manager; Project assurance; Change authority).

As the Project Board (according to PRINCE2) is responsible for the communication between the project management team and stakeholders external to that team, the needed solution can consist in maintaining the role and position of the Monitoring Committee from the NIKM 1st stage also for the 2nd stage of the project (see table 2 – right hand column).

Tab. 2. A comparison of Steering bodies structures of the 1st a 2nd NIKM stage and PRINCE2 principles

1st stage NIKM *- members*	**2nd stage NIKM (draft project)** *- members*	**PRINCE2 roles and responsibilities** *- members*	**Proposal of Modified Steering bodies of the 2nd stage NIKM** *- members*
Monitoring committee - *MoE*[2] - *other ministries* - *regions,* - *SEF/OPE*[3] - *other stakeholders* - *Project manager*	**MoE Control and Monitoring Committee of programmes and projects** - *MoE*[2] - *Executive (CENIA)* - *Project manager (CENIA)*	**Project Board** - *Executive* - *Senior user* - *Project manager*	**Project Board (MoE Control and Monitoring Committee)** - *MoE*[2] - *Executive (CENIA)* - *Project manager (CENIA)* **Monitoring committee** - *Executive (CENIA)* - *Senior user* - *other Stakeholders*
Coordination committee + Inspection day - *MoE*[2] - *SEF/OPE*[3] - *Project manager*	**Management committee** - *Executive (CENIA)* - *Project manager (CENIA)* - *MoE*[2] - *SEF/OPE*[3] *Suppliers*	**Executive** - *Senior user* - *Senior supplier* - *Project manager*	**Executive (committee)** - *Senior user* - *Senior supplier* - *Project manager*
Realization committee - *Project manager* - *Suppliers*	**The main project team**	**Project manager** - *Team manager* **Change authority** **Project assurance**	**Project manager (committee)** - *Change authority* - *Project assurance* - *Team manager*
Workshop (Brainstorming seminar)	**Technical working group**	**Team manager**	**Project teams (working groups)** **Team manager**

Notes: [1] see also http://en.wikipedia.org/wiki/PRINCE2; http://www.prince-officialsite.com/home/home.aspx
[2]MoE: Ministry of the Environment, [3]SEF/OPE: State Environmental Fund/Operational Programme Environment

CONCLUSIONS

The expected outcome of the implementation stage of NIKM is the inventory for the territory of the whole country, but edited into 14 regional reports. The proposed incorporation of the Monitoring Committee into the executive structure of the steering bodies (Project Board) can provide support, besides the intensive communication and the obtaining of help for the information campaign, continuous critical review and feedback from future users – regional offices and other institutions and bodies of the public administration. We expect that during the course of the project, the experience and expertise of stakeholders' representatives can contribute to the supervision of the project. Including stakeholders into the process is clearly a win-win solution.

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CONTAMINATED SOILS IN GEORGIA

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1. Land resources are limited in Georgia. The territory of the country (without territorial waters) is 69,700 km$^{2.}$ According to 2005 data, the total area of agricultural lands is 30,200 km^2 of which cultivated lands (arable lands and land under perennial crops) account for 10,700 km^2. Land in Georgia is divided into two legal categories, land designated for agriculture (40 %) and land designated for non-agricultural purposes (60 %). The latter includes state and municipal forests, protected areas, land covered by water, urban and industrial areas, and land under roads and other infrastructure.

2. Georgia is rich in mineral resources. Uncontrolled and unregulated extraction of mineral resources can significantly impact the environment.

3. Georgia's mineral resources are very important asset for the country's economy. The mining and extraction of mineral resources occupy a leading role in the economy. In Georgia, all mineral resources are the property of the state. Any activity connected to the exploitation of mineral resources is subject to licensing. A license for the exploitation of mineral resources must be obtained through the public auction. The license term depends on the type of mineral resource and on the actual demand for it. In addition to a mining license, the licensee also obtains a temporary right on the land use necessary for the processing operations.

4. The pollution of air, water and soil, as well as deforestation and landslide activation are major environmental concerns related to the extraction of mineral resources. The scale of these impacts varies depending on the minerals being extracted and the technologies used. The anticipated lifetime of mining operation is mainly dependent on the supply of mineral reserves available at the mining site and the viability of their extraction. The rate at which such reserves may be extracted is also determined by the mining license, which defines annual extraction amounts. The terms for mining licenses are set according to the types of mineral wealth and range from 2 to 45 years. In general, the exploration and extraction of metals and solid fuel resources requires much more time than that for construction materials for example, as a result the terms for such licenses tend to be longer.

5. Among the mining enterprises currently operating in Georgia, one of the significant sources of environmental pollution is the extraction of manganese (city Chiatura). For example in January 2009, the concentration of manganese in the river (Kvirila) at the city was 3.9 mg/l, while the maximum allowed concentration is 0.1 mg/l. The area downstream of the extraction facility, including the river and adjacent lands, was tested as contaminated. The situation is aggravated by the fact that background manganese levels are high in the river as it naturally erodes manganese-containing rocks while flowing through the area.

6. Activities connected to poly-metal ore extraction are also very harmful to the environment (Bolnisi). The ore is extracted by open cast mining. The open pit has already been excavated to a depth of 300 meters below ground level. Mining activities such as rock breaking and blasting, in addition to ore moving related traffic, give rise to significant air pollution. Dust clouds travel long distances from the mine, particularly the small dust particles. Additionally, heavy metals are washed out by rainfall, resulting in the contamination of soil and ground waters.

7. In addition to the ore mining, the ore processing operations also have a negative impact on the environment, an example of which is the pollution of the river (Kazretula). This river has been polluted for many years by the activities of mining and processing operations. The primary pollutants are heavy metals. Another nearby river (Mashavera) is partly polluted too, but has self-treatment capacities; therefore maximum allowable concentrations are very rarely exceeded. The area in which waste from the mining process was stored (the tailing ponds) is contaminated with metal wastes including copper, zinc and iron sulphates. In the absence of substantial remediation measures this area cannot be used for agricultural or other purposes, and will remain a contaminated site.

8. Mines that have temporarily ceased operation also have a significant impact on the environment. These sites are temporarily closed and conserved, possibility of contaminating substances spreading from the sites, through ground waters infiltrations, for example still remains. The situation becomes more important when we discuss potential spreading of mercury, arsenic and other substances' from the mining and extractive sites.

9. There are concerns regarding the arsenic extraction works at the mountainous regions of the West Georgia (Lukhuni-realgar-auropigment deposit and Tsana-arsenopirit deposit). Although these industries have temporarily ceased operating, during their operation, pollution from improper extraction and processing operations posed a significant risk to people's health and the environment. High purity arsenic for semiconductor systems and 16 other arsenic containing compounds were produced in these regions (Racha, village Uravi and Svaneti, village Tsana) of Georgia up until the 1990's. The purification process involved the burning of arsenic concentrates in special furnaces, the emissions from containing high concentrations of arsenic sulphides, so called "white arsenic". These emissions impacted an area of more than 20 km around those furnaces. These facilities have now ceased operation, however recent scientific studies found that the content of arsenic in the soils around the factory were 20 to 30 times higher than those of background levels. Increased levels of oncological diseases have been observed among people and domestic animals in the surrounding areas. It is widely held by the local residents that pollution of the rivers (Madnis Ghele, Lukhuni, Tskheniswkhali) and river valleys has resulted in decrease of number of bees and migrating birds in the region.

10. In addition to the pollution caused by emissions from the facility, there are considerable amounts of hazardous wastes stored at these facilities (the tailing ponds), which were generated during their many years of operation. There is an urgent need for proper decommission of these facilities and hazardous waste disposal, including contaminated soil, in an appropriate and environmentally sound manner.

11. The current environmental situation of the deposits and mines within the territories temporarily outside of Georgian Government's control is largely unknown. The main facilities of concern include deposits in South Ossetia (Qvaisi Lead-Zinc) and within Abkhazia (Tkvarcheli coal deposit and Mercury deposits in Akhei and Avadkhara).

12. The extraction and processing of ceramic, semi-precious, inert and construction materials are less harmful to the environment. However when improperly managed, these practices may give rise to significant environmental pollution. The main environmental risks associated with such facilities include the runoff of sediments and contaminated waters into rivers, noise and vibration, particularly associated with blasting at quarries, and dust from the processing and associated transport activities. All of these environmental impacts must be controlled by appropriate legislation and the implementation of an adequate permitting and monitoring process.

13. Waste is a significant source of environmental pollution. The existing legislation, the Law of Georgia on the "Environment Protection" requires that preference be given to the use of recyclable materials and technologies for minimization of waste, when undertaking any kind of activities. It is prohibited in Georgia to dispose of waste by dumping into the sea or in any other water body.

14. The generation of industrial waste in Georgia is not recorded at the moment, and the amount of industrial waste produced annually is not available. According to assessment data prepared in 2006, a minimum of 100,000 tons of industrial waste is produced annually in Tbilisi alone, of which over 6,000 tons are hazardous wastes. During 2007, information was collected from 450 large and medium size enterprises concerning the amounts of accumulated wastes at their sites. This information showed that the total amount of this type of waste was estimated at over 12 million tons, of which 140,000 tons were considered hazardous wastes.

15. There are no landfills for industrial waste in the country. As such, industrial wastes are disposed of at municipal waste landfills, or more often, stored at the site of the facility producing the waste.

16. As mentioned above, during the Soviet era, when the industrial sector operated at full capacity, the mining industry (including coal mining and processing), ferrous and non-ferrous metallurgy and oil extraction/processing were the most significant waste generating sectors. As a consequence, large volumes of industrial waste have been accumulated in the cities where these activities were undertaken. The wastes generated by these industries (ore, untreated rocks, gobs, etc.) were generally stored at the factory site or on lands adjacent to the factory. The wastes were stored at sites without taking into account any environmental considerations.

17. There are 69 official municipal landfills operating in Georgia today. Only two landfills are sanitary landfills meeting the environmental requirements. Environmental requirements are not met by other landfills and they do represent the source of contamination. Besides, there are also other small and medium size landfills also representing contamination risks:

- Some of the landfills are located at or close to riverbanks. During rain and floods waste is washed into the rivers; the landfills do not have drainage system causing the underground water contamination.
- Monitoring of the landfills and their surrounding area, among them of soil is not conducted; The total area of the known landfills is between 289 and 300 ha.

18. It is the provisional to have properly and in environmentally sound manner constructed and managed landfills and other waste management infrastructure.

19. Georgia is party to several international treaties regulating wastes and the use of chemical substances dangerous for the environment. These treaties are:

- The Vienna Convention on the “Protection of the Ozone Layer” (1985) and the Montreal Protocol on “Substances That Deplete the Ozone Layer”. In accordance with these treaties, Georgia is obliged to phase out the production of a number of substances believed to be responsible for ozone depletion. Georgia joined both the Convention and the Protocol in 1996.
- The Stockholm Convention on “Persistent Organic Pollutants”. Georgia joined the Convention in 2006. The convention obliges the countries to neutralize-liquidate persistent organic pollutants occurring as wastes, to reduce to the maximum extend the use of POPs in production with the final aim of phasing them out. Also, reduction of by-products emissions into the environment.
- The 1998 Rotterdam Convention on the “Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides”. Georgia joined the convention in 2007.
- The 1989 Basel Convention on the “Control of Transboundary Movement of Hazardous Waste and Their Disposal”. Georgia ratified the convention in 1999.

20. Pesticides are not manufactured in Georgia. The import of those pesticides as specified banned by the Rotterdam and Stockholm Conventions is prohibited at a national level. There are no reported incidents of illegal import or sale of these substances. However, there are large stockpiles of obsolete pesticides remaining since Soviet period.

21. An inventory of obsolete pesticides held in the country was conducted between 2004 and 2006 with the support of UNDP. Over 3,000 tons of obsolete pesticides have been inventoried, the majority of which (up to 2,700 t) were buried in the depository of chemical substances at the Iagluja Mountain, and approximately 360 tons, in other storage facilities (former Kolkhozes) in different parts of the country. Over 200 of these storage facilities have been assessed, and pesticides were found at 46 of them. During the inventory, most of the storage facilities were damaged; some were completely ruined and robbed (the construction materials were stolen). In many cases the residue pesticides were mixed and dumped in the open air without any packaging. They were exposed to the elements and were being continually washed into the soil.

22. During 2006-2009, most of the obsolete pesticides found in these storages sites (Soviet Kolkhozes) have been collected. Over 230 tons were packaged in containers and removed for storage at the Iagluja Mountain depository. 600 tons of pesticide-contaminated soil was also collected at the former Kolkhozes areas and moved to the Iagluja depository. There are currently only small portions of obsolete pesticides left at different locations within Georgia yet to be collected and safely stored. It should be mentioned that the part of the former Soviet storage and surrounding territories are contaminated, though the contaminated territory inventory or their thorough evaluation has not been conducted. Respectively, there is no draft and approved action plan regarding the contaminated territories in the country.

23. Persistent organic pollutants (polychlorinated biphenyls) are found in Georgia in electrical energy distribution equipment, such as transformers, capacitors, currency-switches etc. There are approximately 1400 tons of oils polluted with polychlorinated biphenyls being in use in Georgia. In order to prevent pollution of the environment, those oils are to be collected and treated using environmentally safe technologies.

24. Thus, the soil contamination is a problematic issue in Georgia and it demands development and implementation of respective activities. More specifically, it is needed to conduct the countrywide inventory of contaminated territories (assessment and evaluation of contaminated areas and the contamination severity and geo information data base creation and others) and to develop and later implement the cultivation plans and project.

25. Similarly, there should be preventive measures undertaken to prevent future potential contamination (conserving old landfills, construction and operation of new landfills in line with modern environmental requirements, introduction of modern technologies among mining and extractive industries, waste minimization and recycling of existing and stored wastes and others). Some other respective activities are already ongoing in Georgia on legislative and strategic planning levels. Additionally, the country is implementing various projects ensuring the capacity building and reduction of contamination and pollution risk factors.

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KEYSTONES IN THE DEVELOPMENT OF THE CONTAMINATED LAND POLICY – TWENTY YEARS WORKING ON CONTAMINATED LAND IN THE BASQUE COUNTRY

Ana Alzola Echazarra

The activity in the sphere of contaminated land dates back to the early 1990s in the Autonomous Community of the Basque Country (CAPV), when different circumstances brought to light the existence of an environmental problem which had remained ignored up until then.

In order to set the context of that time, different cases of land contamination with different repercussions emerged in the CAPV at the end of the 1980s. These included the explosion at a car dealership caused by gases emissions from a hydrocarbon dump of a nearby petrol station that resulted in injuries, the appearance of hazardous and toxic waste, including waste from the production of lindane pesticide, on different land that would be occupied by infrastructures then deemed to be strategic (extending a runway at Loiu Airport or the construction of the first shopping centre) or detecting gases in households whose presence was found to be related with contaminated sites.

The first reaction was to try and solve the cases as they emerged. However, what was occurring in the CAPV mimicked something that had been experienced only a decade earlier in other countries. The cases of Lekkerkerk (The Netherlands) in 1978 and Love Channel (USA) in 1979 are famous. These two cases, along with others that occurred in Germany and Denmark, for example, at the end of the 1970s, forced these and other countries to embark on specific policies in anticipation of what would be required regarding the problem.

This would be the same sensation as the one experienced in the Basque Country; the cases that had cropped up would be no more than a tip of the iceberg in a country with a long industrial history and a territory where the residential, industrial and other land uses had been intertwined over the years. One of the consequences of the budding urban regeneration process at the end of the 1980s and the subsequent "frenetic" years could have been the appearance of risks, some of which would be unacceptable for human health, when new uses were established for land previously for industrial activities or for dumping their waste. One only had to look around and at the first waste inventory that was completed in 1989 to confirm that. Something that back then was only a vision has been confirmed by the work subsequently performed.

Thus, between 1991 and 1992, at a time when the contaminated land was still not in the social nor the political debate, nor even in the technical debate, the CAPV took the initiative to address a strategy in a new environmental field: contaminated land.

THE FIRST STEPS

Faced with a problem on a then unknown scale, a strategy outline was prepared to protect and recovery of the soil quality that was embodied in the ***Guidelines to Prepare the Master Plan to Protect Contaminated Land*** (March, 1992) presented at the I International Conference on Contaminated Land, an event that together with its second edition showcased the latest trends and concepts at that time.

These guidelines were set out in a simple document, with a limited scope regarding its contents. However, time has shown that the line it took was the correct one, both as regards the type of lands that would be the core areas of the contaminated land policy and the areas where measures would need to be taken. Landfills and derelict industrial areas (industrial ruins) were then identified as the most significant focal points. The guidelines already found the key words of what the contaminated land policy in the CAPV has been and what it must be: the need to assess the size of the problem, the role of the specific legislation in this area, the importance of scientific and technical knowledge (in research and recovery of contaminated land), the interrelation of soil quality with the land planning process, the setting up of an organisational structure and a budgetary allocation to implement this new policy and, of course, preparing a plan including all those aspects and all those that emerged from a more detailed study.

The two years that followed the drafting of the guidelines were very intense; a work team was set up for the exclusive purpose of drafting a master plan in line with the needs and possibilities of the CAPV, which required parallel work in very different areas. The initial work focused on the following aspects:

- *Quantification of the size of the problem*. One of the first goals of the work team was to prepare a preliminary land inventory that had been used for potentially contaminating activities that would be used to scale the scope of the solutions.

- *State-of-the-art study*. Apart from the support provided by the experts of different countries, the work team studied all everything that had been published on contaminated land from the technical, legal and administrative perspective.

- *Work started on preparing specific contaminated land legislation*. Even before a master plan was drafted, work had already begun on preparing a legal text that would finally become the *Land Contamination Prevention and Remediation Act 1/2005 (Ley 1/"005, de prevención y corrección de la contaminación del suelo),* a key element given as the driving role that legislation plays.

- *Derivation of soil quality standards*. The contaminant concentrations were then unknown that would indicate the need for action to be taken where the quality of the land is impaired and even the characteristics of the natural soils of the Basque Country. It was therefore obvious that the establishing of these concentrations had to be one of the first tasks to be undertaken

- *Development of the first technical guides*. Measures for contaminated land require technical knowledge to research and subsequently recover this resource, which did not exist at local level at that time. In order to generate knowledge to be transferred to Basque consultants and laboratories and for them to establish a uniform criterion in areas such as the designing of research strategies, sample taking, the analysis of contaminants or risk analysis, work began on preparing specific document in this and other fields. The obvious interest of these guides has meant that they remain a fundamental line of work in the CAPV**.**

This initial work enabled the sufficient degree of knowledge to be generated to underpin the ***Master Plan for Land Protection*** that was unveiled in September 1994 during ***II International Conference on Contaminated Land***. The experience of the Basque Country was very limited at that time. However, this conference and subsequent interventions in other international events, led to the Basque Country being recognised as a region that was endeavouring in order to solve the problems of contaminated land. The Basque Country therefore had the opportunity to join work groups that have set European polices including CARACAS (Concerted Action for Risk Assessment for Contaminated sites in Europe), CLARINET (Contaminated Land Rehabilitation Network for environmental Technologies in Europe) or the Common Forum on Contaminated Land in Europe. The integration in those groups enabled, first of all, first-hand monitoring of the cutting-edge management of contaminated land, secondly, the opportunity to discuss areas of special concern in the CAPV and, finally, increase the degree of international recognition.

The *Land Protection Plan* governed the contaminated land policy for a long period time; it established the framework and drew up the guidelines, mainly focused on data acquisition and on preparing instruments. In parallel, a growing trend was noted in research and land recovery by private initiative to which a response was needed from the administrative sphere where there was no specific legislation that regulates the declaration of the quality of the land for this sector. Due to the private asset nature of the land, the measures regarding contaminated soils were not only driven by the legislation but also by the market forces.

Fig. 1. Historical trend of the land surface area of the Autonomous Community of the Basque Country recovered for new uses during the last decade (Source: Ihobe).

THE CONTAMINATED LAND PLAN 2007-2012

The period following the 1994 Master Plan was when a broad range of parallel and interrelated work was embarked on; the data in the successive inventories helped to quantify the size of the problem and therefore, they affected planning; the actions at specific sites provided information about the different case loads and way of providing solutions, which was fundamental to draft legislation or to develop methodology guides adapted to the reality of the Basque Country.

Since 1994, the level of knowledge and experience in the Basque Country has increased significantly. The concepts guiding land protection worldwide had been expanded on the way towards sustainability and the land protection policy required from a new time of reflection in the light of the new circumstances. It must likewise not be forgotten that *Land Contamination Prevention and Remediation Act 1/2005*, establishes the obligation of the environmental authority to prepare a contaminated land plan in order to define: the strategic guidelines, the action needs for the period it is in force, the instruments for their implementation and the list of action priorities regarding the risk to the health of the people and the environment from the contamination.

Consequently, the ***Contaminated Land Plan 2007-2012*** was ratified by the Government Cabinet on 27 December 2007. The following table summarises the actions included organised in three programmes and nine lines of action.

PR 1. EZAGUTU PROGRAMME: AWARENESS RAISING, INFORMATION, TRAINING AND RESEARCH	
LA.1 Compilation, organisation and management of the information relating to the soil quality	
	A.1.1 Adapting to the needs of the moment and managing a system of soil quality information
	A.1.2 Keeping the information relating to the soil quality up to date
L.A.2 Knowledge generation	
	A.2.1 Creating permanent multi-disciplinary work teams in different fields
	A.2.2 Reinforcing the science and technology policy to generate knowledge
LA.3 Awareness raising, information and training	
	A.3.1 Communicating and disseminating key aspects related to land contamination
	A.3.2 Increasing know-how among the stakeholders involved in land management
	A.3.3 Structuring decision-taking participation mechanisms
PR 2. ERAGIN. STRUCTURED ADMINISTRATION	
L.A.4 Optimising the performance of the environmental authority and the application of the contaminated land legislation	
	A.4.1 Updating, improving and simplifying the application of the legislation, addressing the soil quality declaration procedure.
	A.4.2 Ensuring compliance of the legislation
L.A.5 Creating appropriate partnership conditions between the different levels of the administration to anticipate the intervention in contaminated lands	
	A.5.1 Integrating the land protection policy in other policies
	L.A.5 Creating appropriate partnership conditions with the stakeholders to anticipate the intervention in contaminated lands
PR 3. EKIN: PREVENTING, RECOVERING, REUSING AND ENHANCING	
L.A.6 PREVENTING the appearance of new contaminated land	
	A.6.1 Driving preventive measures using administrative tools
LA.7 ***Searching for solutions for the RECOVERY of contaminated sites***	
	A.7.1 Driving the creation of infrastructures for the recovery/management of contaminated land
	A.7.2 Designing and applying economic instruments that drive the recovery of contaminated land
	A.7.3 Developing and applying the risk management concept in its most advanced accepted forms
	A.7.4 Defining criteria for the reuse of recovered land and excavated materials at sites affected by contamination
L.A.8 REUSING unoccupied sites and whose quality has been affected	
	A.8.1 Preparing guidelines and identifying measures to reduce the artificialisation of the land
	A.8.2 Using urban development to facilitate the reuse and recovery of contaminated land
L.A.9 Managing potentially contaminated land without planned urban development actions ENHANCING	
	A.9.1 Designing and implementing strategies for action at potentially contaminated sites outside the urban development market

Between drafting both plan, significant progress was made in all the fundamental areas that require a structured contaminated land policy. Some of the most important are outlined in the following paragraphs.

LEGISLATION REGARDING CONTAMINATED LAND IN THE BASQUE COUNTRY

The first guidelines to prepare the master plan already identified legislation as a fundamental driving force in the area of contaminated land, even though it would take a further ten years for the Basque Country to have the first specific standard in this area. However, time has shown that the systematization work on which the legislation is based would not have been possible without the acquired experience during those years between the approval of the *General Environment Act 3/1998 (Ley 3/1998, general de medio ambiente)* and Act 1/2005.

The work to draft the legislation that had already begun at the start of the 1990s saw its first results with the incorporation of the first concept to protect the land and the management of the contaminated land into the *General Environment Act 3/1998 of the Basque Country* . However, the articles dedicated to this area in the General Act did not go any further than a declaration of intentions supported by a series of general principles.

The first key legislative milestone was the coming into force of the *Land Contamination Prevention and Remediation Act 1/2005, of 4 February*, which currently regulates the measures taken in the prevention of contamination and in the management of contaminated land in the CAPV. Practically simultaneously, *Royal Decree 9/2005, of 14 January, which established the list of potentially land contaminating activities and the criteria and standards for the basic declaration of contaminated sites* was approved (*Real Decreto, 9/2005, que establece la relación de actividades potencialmente contaminantes del suelo y los criterios para la declaración de suelos contaminados*).

Today, six years after its approval, it can be considered that the degree of application of Act 1/2005 is greater than the average of the other environmental legislation. This success is down to several factors, where special mention should be made of the clear identification of the cases where the declaration procedure of the soil quality is required (installation of new activities, change of use, soil movements, contamination indexes, etc.) and the express prohibition of granting planning permission on potential contaminated land without the presence of the soil quality declaration.

The application of the law has enabled important fields for improvement to be identified, particularly with regard to simplifying the administrative formalities and to establishing the ways of doing things for the different cases that may arise. The outcome of this pragmatic assessment is that work is currently being carried out on the preparing of draft amendments that will help to increase the flexibility and the proportionality between the probabilities of changes to soil condition and the obligations imposed in each case.

Act 1/2005 already identified the fundamental aspects that would have to be developed statutorily to facilitate their application. These included: the accreditation system for entities specialising in investigation and remediation of contaminated land, the content and scope of the investigation on which the soil quality declaration and the inventory of potentially contaminated land are based. In order to endow these matters with content, two enactment provisions were approved: ***Decree 199/2006*** *which established the system for accrediting soil quality research and recovery entities and determine the content and scope of the soil quality research to be carried out by those entities (Decreto 199/2006, que establece el sistema de acreditación de entidades de investigación y recuperación de la calidad del suelo y se determina el contenido de las investigaciones de la calidad del suelo a realizar por dichas entidades)* and ***Decree 165/2008,*** *of 30 September, of land inventorie used or which have been used for activities or installations that potentially contaminate land (Decreto 165/2008, de inventario de actividades e instalaciones que soportan o han soportado actividades potencialmente contaminantes del suelo).*

THE SOIL QUALITY INFORMATION SYSTEM

The information on the soil quality is another of the pillars underpinning the contaminated land policy to:

- *Estimate the size of the contaminated land problem to design* both general and partial/sectoral strategies (abandoned landfills, sites in sensitive zones, etc).
- *Identify those lands where there is a risk of contamination requires the implementation of the soil quality declaration procedure*. The potential contaminated land inventory is a basic tool for the administrations and, in particular, for the local councils which Act 1/2005 requires not to grant licences for potentially contaminated land without the relevant declaration.
- *Register all the data obtained pursuant to the contaminated land legislation or other land measures*. As Act 1/2005 recognises, there is the need to centralise all the available information on the soil quality of all the (potentially) contaminated plots. This information, apart from underpinning the policies of the administrations, guarantees the legal safeguards of the parties concerned that can access it in the terms laid down by law regarding access to environmental information.

The forerunner to the 94 Master Plan carried out initial estimations based on a preliminary inventory of potentially contaminated land that would act as the basis for the 1994 master plan. The forerunner calculated that the number of plots included in this category would be around 2,000-3,000, out of which 664 were landfills and 474 industrial ruins, which had already been subject to an exhaustive inventory process. Six years would have to pass before the detailed inventory would be completed of all the municipalities of the CAPV, an inventory that already included 8,585 plots that covered 8,435 Ha. The latest updating of the inventory, still in the phase of integration, envisages over 12,000 plots on a surface area that exceeds 9,000 Ha.

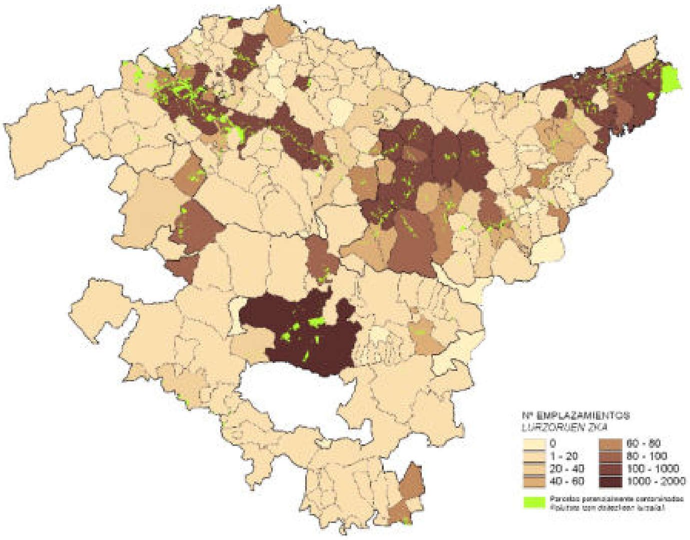

Fig. 2. Distribution by municipalities of the potentially contaminated land in the Autonomous Community of the Basque Country (Source: Ihobe).

As regards the types of site, it is interesting to take into account, due to their differentiated treatment, both from the technical and legal perspective, that 10% are landfills while the result that have been in the past or are in the present occupied by industrial activities.

Three interrelated instruments have been developed in the Basque Country to manage the information relating land quality: the inventory of sites with activities and installations that potentially contaminate land, the Soil Quality Administrative Registry and the Soil Quality Information System:

- **Inventory of potentially contaminated land.** The inventory identifies and locates in the territory all those plots on which the potentially land contaminating activities included in Act 1/2005 have been or are being carried out. It is information gathered through research in archives, checking with municipal technicians and field visits. The inventory is an instrument of great importance as the fundamental obligations of the Act 1/2005 are linked for certain circumstances to occur (change of use, excavation, installation of new activities, etc.) on those plots.

- **Soil quality administrative registry** The registry contains all the information obtained pursuant to Act 1/2005 in order to guarantee the legal safeguards and the public information. The aim is to make the data existing on each plot available to the general public in a centralised way so that when they show any type of interest, they may resort to this registry for information on this possible environmental load.

- **GEOIKER soil quality information system**. This system, which combines a database with an GIS, is used to store and manage the information on soil quality. It contains both the information from the inventory and from the registry, and from other sources such as the preliminary status reports. Apart from the supporting the soil quality declaration procedure, the system enables the overlapping with other thematic layers that may help to interpret the available information (aquifer vulnerability, natural spaces, geology, etc.) and is the basis to design customized web services.

Fig. 3. Graphical overview of the information sources of the Soil Quality Information System.

At the time of writing, the only information that has been published has been the Inventory of Potentially Contaminated Land that can be consulted through the Information System of the Basque Government, Geoeuskadi. However, different groups have expressed their interest in more advanced information to which they could be allowed to access: local councils, administered and accredited entities and other administrations. By way of an example, work is currently being carried out on making the inventory update available to the public through a website service that allows each local council to see and amend the data relating to its territory.

DEVELOPMENT OF MANAGEMENT AND TECHNICAL TOOLS. LOOKING TOWARDS THE FUTURE

As has already been mentioned, it was considered essential right from the start to generate knowledge and prepare instruments that are in keeping with the situation and possibilities to act in the Basque Country. The first methodological guides emerged from this need which underpinned the procedure to research and recover contaminated land. Soil quality standards, historical survey and sampling designs, sampling, chemical analysis and human health risk analysis and the eco-systems were the first. Others were subsequently published such as the risk analysis for underground waters, occupational safety in research and recovery of contaminated land or the environmental criteria for action in industrial ruins. They are all still very topical today.

The formula of publishing methodology guides continues to be in force in order to provide uniform and coherent responses to the problems that emerge. Thus, there are several that are currently in the development and publication process:

- Guide to carrying out excavation work in sites where the soil quality is altered.
- Guide to assess the tools used to evaluate the pollution of underground water from land contamination.
- Guide to assess pollution from oil hydrocarbons.

COOPERATION WITH OTHER ADMINISTRATIONS

The *Contaminated Land Plan 2007-2012* identifies cooperation with other administrations as one of the priority lines of action of the programme. It is pointless to address the actions on contaminated sites exclusively from the environmental perspective when there are so many other aspects that affect land management. In the Basque Country and so far, the cooperation with other administrations has been from two areas:

- *Cooperation aimed at the integration of land protection criteria in other policies*. The policy to protect land against contamination requires good inner workings with other policies to achieve the goals set by the plan. Therefore, the Basque Country is proposing the setting up of cooperation agreements between administrations with complementary spheres of action. During that period, integration has begun in urban development, food safety and the protection of underground water.
- *Support for the research and recovery of specific sites or spheres*. Our administrations require the technical support of the Environmental Office and of Ihobe, the Environmental Management Agency, to investigate and remediate sites where interest is expressed to act for different reasons. The local councils and the economic and technical support offered by way of aid from the Department for the Environment and Spacial Planning to local authorities must not be forgotten. .

THE ADMINISTRATIVE PROCESSING OF THE SOIL QUALITY DECLARATION

An important part of the contaminated land policies is related to the administrative processing of the soil quality declaration and everything surrounding it. The most significant tasks of the processing are as follows:

- *Answering queries*, where it has answered in recent years an annual average of 600-700, of two types:
    - Prior queries regarding the administrative or technical requirements of the declaration pursuant to Act 1/2005.
    - Queries to the Soil Quality Administrative Registry by means of Geoiker, the Soil Quality Information System.
- *Rulings on soil quality declaration cases*. In 2010, the number of open cases involving some type of processing was 220.
- *Accreditation of entities specialising in research and recovery of contaminated lands* . Pursuant to Act 1/2005, the research and recovery of contaminated lands that is carried out in the sphere of application of that legislation must always be implemented by entities that have been expressly accredited by the environmental authority. There are currently approximately 40 accredited entities.

THE FUTURE

It is difficult to foresee the future in an economic crisis such as the current one. However, the experience of recent years provides at least a glimpse of some of the challenges that we will have to face.

Once embarked on the way to solve the problems of sporadic contamination, the need emerges to go further towards the diffuse awareness of contamination that, although with less intensity, may be affecting water resources, agricultural products of the operating of the eco-systems.

Soil is increasingly being recognised as the support for life on the planet and its functions as regulators of innumerable life processes. Its preservation from all perspectives, not merely from the fight against contamination, but also more in keeping with the sustainability concept, will direct the endeavours towards a more holistic concept where soil health will replace soil quality.

Yet that cannot all occur within the fundamental work of awareness-raising of administrations and the general public that still do not realise the importance of having healthy soil has for all the beings living on this planet.

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MONITORING OF CONTAMINATED SITES OF SELECTED AREAS IN THE SLOVAK REPUBLIC

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INTRODUCTION

In December 2000, Directive of the European Parliament and of the Council 2000/60/EC establishing a framework for Community action in the field of water policy(in short called the Water Framework Directive – WFD hereinafter) was accepted, which provides a legislative framework for comprehensive protection of all waters within the territory of the European Union. The WFD is closely related to the implementation of the obligation of the subsidiary Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration.

In the context of a comprehensive water protection it is also necessary to address point sources of pollution (so called contaminated sites). Fundamental principles of the solution of contaminated sites are derived from the integrated water management strategies enshrined in the WFD. Ministry of Environment of the Slovak Republic, as Managing Authority for the Operational Programme Environment, on 06.09.2012 decided to approve an application for grant titled „Monitoring of contaminated sites of selected areas of the Slovak Republic“, which is nowadays realised by the State Geological Institute of Dionyz Stur (SGIDS). The aim of the project is to design and implement the monitoring systems for selected contaminated sites in Slovakia. The project meets the program objectives of the Government of the Slovak Republic, which are defined in the document „National Contaminated Sites Remediation Program 2010-2015“. The project is built on the results of past departmental tasks of the Ministry of Environment (MoE), especially the projects: „Systematic identification of contaminated sited in Slovakia“ (Paluchová et al., 2008), „Regional Environmental Impact Assessment Studies of the Contaminated Sites in Selected Regions - Slovak Republic“ (Helma et al., 2010) and „Project completion of information system of contaminated sites“.

Objective of the project carried out by SGIDS will be achieved by the implementation of the following activities:

- processing of archival materials,
- build conceptual models and their updating,
- design a monitoring program and its update,
- implementation of monitoring – sampling, field measurements and laboratory work,
- modeling and evaluation of monitoring results.

Those activities are in accordance with standard practices in the EU and in accordance with the WFD, respectively its Daughter Directive on the protection of groundwater, which constitute the basic legal framework for the implementation of this project. In this paper, a basic information about the project is presented.

BACKGROUND OF THE PROJECT – LEGAL COMPLIANCE AND STRATEGIC DOCUMENTS

The project is in line with the EU legal framework, national legislative framework and national strategic and regional documents on the environment, respectively. A short characterization of important documents and issues for the project implementation is listed below.

Directive 2000/60/EC of the European Parliament and of the Council of 28 October 2000 establishing a framework for Community action in the field of water policy

The Water Framework Directive establishes a legal framework to protect and restore clean water across Europe and ensure its long-term and sustainable use. The directive establishes an innovative approach to water management, which is based on river basins, natural geographical and hydrological units and establishes specific deadlines for Member States to achieve ambitious environmental goals in aquatic ecosystems. The directive addresses the issue of inland surface waters, transitional waters, coastal waters and groundwater.

Article. 4 of the WFD provides for groundwater following environmental objectives, which is to be assumed in the design of program actions:

- introduce the necessary measures **to prevent or limit inputs of pollutants into groundwater** and to prevent the deterioration status of all groundwater bodies,
- protect, enhance and restore all groundwater bodies, ensure a balance between abstraction and recharge of groundwater for the purpose of achieving good groundwater status at the latest by 2015,
- take action to reverse any significant and sustained upward trend in the concentration of any pollutant that is caused by human activity, in order progressively to reduce pollution of groundwater.

Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration

The Directive aims to ensure consistent protection of groundwater in the European Union. According to Article 5: Identification of significant and sustained upward trends and the definition of starting points for trend reversals, the paragraph 5 of this Directive underlines the need to assess the impact of existing contamination plumes in groundwater bodies that are caused by point contamination sources and contaminated soil. It is important to identify pollutants in order to verify that plumes from contaminated sites do not expand, deteriorate the chemical status of a groundwater body or group of groundwater bodies and whether they constitute a risk to human health and the environment. Under Article 6: Member States shall establish a program of measures to prevent or limit inputs of pollutants into groundwater.

It is necessary to distinguish between hazardous substances for which inputs should be avoided and other pollutants, which inputs should be limited. Annex VIII to Directive 2000/60/EC, listing the main pollutants relevant for the aquatic environment, should be used to identify hazardous substances and substances that are not hazardous, but actual or potential for risk of pollution.

Input of pollutants to groundwater is direct or indirect introduction of pollutants into groundwater caused by human activity. Inputs are either point sources of pollution from one source discharges/emissions/installation or diffuse sources. The difference between the two inputs is characterized by the number of inputs and the extent to which they occur. Diffuse inputs are mainly associated with agricultural activities, inputs of pollutants from atmospheric deposition to soil (due to air emissions from industry, traffic, fire, etc..) and inputs from large agglomerations (large urban areas). Direct inputs may be assigned one of the following: are outside the zone of aeration (source pollution directly in groundwater), source of pollution in the zone of saturation (or direct penetration of pollutants into the zone of saturation), seasonal fluctuations in groundwater levels causing the pollution source is in direct contact with groundwater only in a certain time period.

Prevent the entry of pollutants into groundwater is meant to take all measures deemed necessary and appropriate to prevent the input of hazardous substances into groundwater and to prevent a significant increase in their concentration in groundwater, even at the local level. Adequate means technically feasible at a reasonable cost. The question is, to what distance (depth) from (potential) source of pollution should be the entry of the pollutant into the environment (groundwater) rated.

In assessing the appropriate measures to prevent indirect inputs of hazardous substances into groundwater should be pursued further depletion of their occurrence (fixation, degradation) in the aeration zone and dilution of pollutants in the direction of groundwater flow. On each of investigated (monitored) site, dealing with contamination, deep information about geological, hydrogeological, hydrogeochemical conditions including the ongoing processes in the system and changes in groundwater levels is necessary to take into consideration.

Protection of groundwater is mainly based on the protection of a wide range of receptors (use of groundwater – pumping, transfer of groundwater to rivers and wetlands etc.). This approach is applicable for the substances to be limited in the groundwater. For dangerous substances, their entry into groundwater must be prevented (groundwater is a receptor as a whole).

Assessment of good chemical status is made at the level of the groundwater body and is carried out periodically every six years (compilation of river basin management plans). Defining good chemical status in the evaluation of groundwater bodies is limited to a few specific receptors and conditions and may not necessarily protect groundwater quality at the local level (e.g. in connection with the assessment of environmental impacts). **To support assessment of groundwater chemical status at local level is a key message of the presented monitoring program.**

Directive of the European Parliament and Council Directive 2006/21/EC of 15 March 2006 on the management of waste from extractive industries and amending Council Directive 2004/35/EC

The Directive aims to adopt a series of measures to prevent the negative impact of waste from mining activities on human health, property and the environment and also measures to prevent the occurrence of major accidents in the management of that waste. The Directive is based on the general provisions of the Waste Framework Directive (75/442/EEC). The Directive clearly defines the requirements to be fulfilled for the waste facility servicing the extractive industries, in order to prevent any threat to the environment in the short and long term and also specific measures against pollution of groundwater by leachate infiltration into the soil.

BASIC PRINCIPLES OF MONITORING PROGRAM

Contaminated sites pose a risk of pollution of groundwater and rock environment. They represent primarily large industrial objects (areas), settlement agglomeration, landfills, mining industry, manufacture of paper and paper pulp processing, metallurgical production etc. Selected contaminated sites for monitoring program in the Slovak Republic are shown in Fig. 1. For large-scale contaminated sites, an important factor is spatial density of point, which result in duplication of contamination sources and the inability to define the input values for the different entities (e.g. large industrial enterprises, residential agglomeration). Sources of pollution in such cases constitute a very heterogeneous set of what the composition of matter, quantity, method of storage and disposal, technical measures, environmental conditions.

Basic issues in the preparation of the monitoring program of contaminated sites are: where, what, when and how often to monitor. The monitoring program is dependent on the objectives of monitoring, the required accuracy and reliability of monitoring results and the type and variability of endpoints. The monitoring program is compiled separately for each site based on the conceptual model. The main principles of monitoring design are as follows:

- must be based on the expected places of leakage of pollutants into groundwater,
- must take into account the directions of groundwater flow,
- at least one observation object is necessary to establish in the area with background natural conditions,
- the frequency of observations and density of the monitoring network must take into account the behavior of pollutants in the environment (eg, time delays, migration properties, the formation of degradation products, etc.),
- monitored indicators should be indicative of the type of pollutant and the proposal for a possible remediation measures (measurement indicator parameters such as redox potential, pH, specific electrical conductivity, temperature, can reduce the extent and intensity of monitoring),
- methods of sampling, storage of samples and analytical methods will depend on the nature of the entry and the expected concentrations of pollutants,
- installation of monitoring wells and depth of monitoring should take into account environmental characteristics, type of pollution and nature of the pollutant input into the system (seasonal fluctuations in water levels, identify potential migration and preferential pathways, solubility/insolubility in water, DNAPL/LNAPL, etc.),
- must be based on cost-benefit analysis of monitoring sites, frequency and extent of observations in relation to expected results.

Monitoring of environmental sites has a local character and plays additional role to national monitoring network program to evaluate the chemical status of groundwater bodies and river basin management plans. The goal of monitoring is to identify contaminated sites:

- whether there is leakage of pollutants into the environment,
- what is the spatial extent and depth of contamination in environment,
- trends in concentrations of pollutants.

Monitoring will contribute to a comprehensive and systemic management of contaminated sites, the gradual removal of contaminated sites and reduction of risks arising from them. The proposed monitoring network is based on the four different points of compliance (POC):

- POC 0 is located at the bottom of the source of contamination in the unsaturated zone,
- POC 1 is located at the level of the groundwater level for checking whether pollutants penetrate into groundwater (zone of saturation),
- POC 2 is located in the direction of the hydraulic gradient between POC 1 and receptors (its aim is to provide early warning that the receptor may be adversely affected),

- POC 3 is used to monitor the impact of pollution in the receptor site.

Number of monitoring sites will essentially depend on the spatial extent of contamination, the number of pollution releases, environmental characteristics of the contaminant (if necessary) and legislative requirements.

In determining the monitoring network, the following steps are proceed:

1. identification of existing or planned receptors,
2. assessment of potential use of aquifer taking into account current and future land use, land ownership, topography, exploitable quantities of water from the hydrogeological structure and the background quality,
3. identification of pollutants and determine the extent of contamination,
4. prediction of impact of the contamination source to groundwater quality,
5. assessment of potential significance of attenuation in reducing contamination,
6. identification of a suitable points of compliance,
7. derivation of compliance concentrations.

The number, location and structure of monitoring sites is determined specifically for each site. It takes into account:

- size of the contamination source,
- type and distribution of contaminants,
- complexity of the hydrogeological structure and groundwater flow,
- access – including existing buildings and services, ownership and security establishment of the monitoring network,
- sensitivity of the receptor at risk
- requirements of regulatory authorities.

ACKNOWLEDGEMENTS

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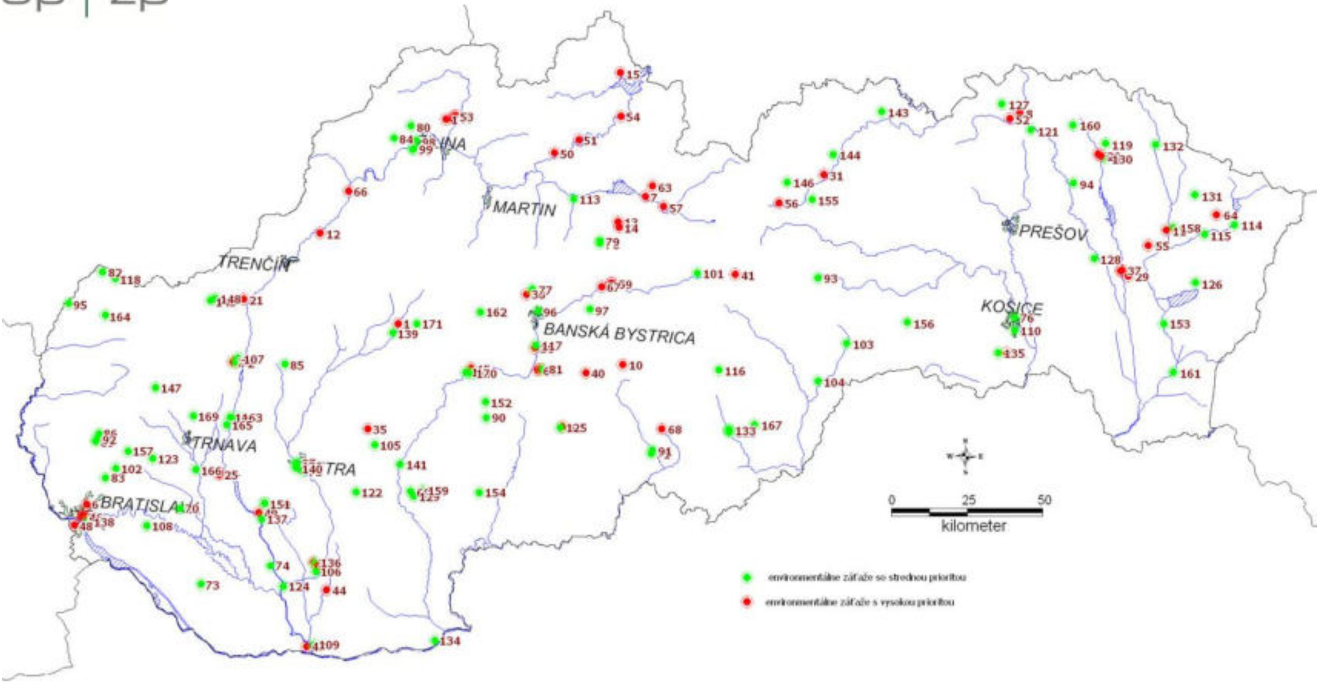

Fig. 1. Selected contaminated sites for monitoring in the Slovak Republic

REMOVAL OF ORGANOCHLORINATED PESTICIDES BY ADSORPTION OZONATION

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KEYWORDS

Chlorinated compounds, ozone/GAC process, ozone/zeolite process, priority and persistent substances, water and wastewater treatment

INTRODUCTION

This paper focuses on the use of ozone for the elimination of selected dissolved organic micropollutants from water and wastewaters. Five selected organochlorine pesticides, i.e. hexachlorobutadiene, pentachlorobenzene, hexachlorobenzene, lindane and heptachlor were used as organic contaminants of model water. The first four of them are classified as priority hazardous substances [1, 2]. Heptachlor (HCH) is a persistent organic pollutant (POP). Due to its highly stable structure, heptachlor can persist in the environment for decades. It has a half life of ~1.3-4.2 days (air), ~0.03-0.11 years (water), ~0.11-0.34 years (soil) [3]. The main problem of this compound is that its derivates can be more toxics than HCH. Heptachlor was designated as a possible human carcinogen by The International Agency for Research on Cancer [4]. Hexachlorobenzene (HCHB) or perchlorobenzene, is a white crystalline solid that has negligible solubility in water. It is a fungicide formerly used as a seed treatment, especially on wheat to control the fungal disease bunt. It has been banned globally under the Stockholm Convention 2001 [5] on persistent organic pollutants. HCHB is an animal carcinogen and is considered to be a probable human carcinogen; increased incidences of liver, kidney and thyroid cancer, skin lesions with discoloration have been diagnosed. Neurological changes in rodents exposed to HCHB have also been reported. It is very toxic to aquatic organism and persistent in the environment. Ecological investigations have found that biomagnifications up the food chain occur. HCHB has a half life in soil of between 3 and 6 years. Also, the risk of bioaccumulation in aquatic species is high. This material has been classified by the IARC [4] as possibly carcinogenic to humans. Hexachlorobutadiene (HCBD) has been classified by the United States Environmental Protection Agency [6] as a possible human carcinogen. It may cause also genetic damage and has been observed to produce systemic toxicity following the exposure via oral, inhalation, and dermal routes. Its effects may include epithelial necrotizing nephritis, central nervous system depression and cyanosis. Pentachlorbenzene (PCHB) is a persistence organic pollutant accumulating in the food chain [7]. It can enter human body by eating or drinking contaminated food and water or by breathing contaminated air. PCHB decomposes on heating or burning with the formation of toxic, corrosive fumes including hydrogen chloride. Combustion of PCHB may also result in the formation of polychlorinated dibenzodioxins ("dioxins") and polychlorinated dibenzofurans. Consequently, PCHB was in 2009 added to the list of chemical compounds covered by the Stockholm Convention [8], an international treaty which restricts the production and use of persistent organic pollutants. PCHB is very toxic to aquatic organisms. It affects the central nervous system; long-term exposure can affect the liver and kidneys and can cause tissue lesions. Animal studies and tests show that PCHB can possibly have toxic effects on human reproduction. Lindane is the gamma isomer of hexachlorocyclohexane ("γ-HCH") that was used both as an agricultural insecticide and as a pharmaceutical intermediate product. It is relatively long-lived in the environment. It is transported long distances by natural processes like global distillation. It is persistent organic pollutant that bioaccumulates in food chains though it is rapidly eliminated when exposure is discontinued [9]. In humans, Lindane affects the nervous system, liver and kidneys, and it is a possible carcinogen [10]. Most pesticides are resistant to chemical and/or photochemical degradation under typical environmental conditions. Among the possible chronic effects of these compounds are carcinogenesis, neurotoxicity and effects on reproduction and cell development particularly in the early stages of life. Monitoring programmes in many European countries demonstrate the presence of pesticides in surface waters ranging from streams and ditches directly adjacent to agricultural fields up to large rivers, lakes and reservoirs. Part of the larger-scale contamination is known to result from non-agricultural uses of pesticides or from point sources, including discharge from farmyards following filling and washing activities. Nevertheless, diffuse contributions of pesticides to water are also important. These are predominantly from pesticides applications including spray drift, surface runoff and leaching to field drains. Less significant routes to surface water include groundwater seepage, subsurface lateral flow and wet or dry deposition following longer range transport in air. Movement via field drains has been shown to be important in a number of countries and rapid transport of pesticide residues in drain flow has been demonstrated in a large number of field experiments [11]. Pesticide pollution of surface water and groundwater has been recognized as a major problem in many countries because of their persistence in aquatic environment and potential adverse health effects. Wastewater treatment plants are designed primarily to eliminate nutrients. However, attention is increasingly being focused on micropollutants, since even low concentrations of these substances can have adverse impacts on aquatic ecosystems. The incapability of biological wastewater treatment to remove effectively hazardous, toxic and biologically resistant pollutants shows that the new treatment processes are needed to be developed. Ozonation of wastewater appears to be a promising tertiary treatment process for removal micropollutants at treatment plants. The improvement of the efficiency of organic pollutants removal was observed in combined systems of ozone with adsorption materials. Zeolite is a natural, low cost, and widely available material, and would be suitable candidate for heterogeneous ozonation [12]. The feasibility of two combinations of ozone with granular activated carbon (O_3/GAC)) as well as with zeolite (O_3/zeolite) were studied for removal of the above mentioned selected organochlorine pesticides.

MATERIAL AND METHODS

Experimental equipment

Ozonation experiments were carried out in a lab-scale ozonation reactor. A scheme of the ozonation equipment is shown in Fig.1. The ozonation reactor was 0.07 m in diameter and 0.2 m in height. Effective volume of the reactor was 0.5 dm^3. Continuous flow of oxygen of 60 dm^3 h^{-1} was applied for the generation of ozone. Ozonation trials were carried out at 50 % of the ozone generator's power maximum.

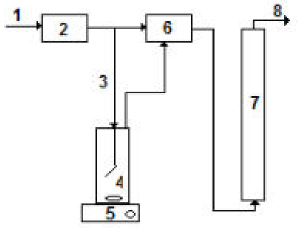

Fig. 1. Schematic diagram of the experimental apparatus

Experiments were performed with model water which contained our chosen chlorinated pesticides, i.e. hexachlorobenzene, hexachlorobutadiene, pentachlorobenzene, lindane and heptachlor. Experiments were carried out in laboratory conditions. Granular activated carbon (GAC) and zeolite were used. 0.100 g of GAC and 1.00 g of zeolite particle fraction d = 0.315 to 0.4 mm was applied.

1 - oxygen, 2 – ozone generator , 3 – O_2 and O_3 mixture, 4 – ozonation reactor, 5 – magnetic stirrer, 6 – ozone detector, 7 - bubble column for residual ozone destruction, 8 – outlet gas mixture

Analytical methods

Quantification of the organochlorine pesticides in water was achieved by Gas chromatographic method after liquid-liquid extraction. n-Hexane 96%, p.a. for HPLC (Analytika, s r.o.) was used as anorganic solvent. Extract was analyzed by gas-chromatography with micro electron capture detector (Agilent Technologies 7890A GC Systems). All parent organochlorine compounds used for preparation of synthetic wastewater and standard stock solutions were purchased from Supelco Co in high quality.

RESULTS AND DISCUSSION

Combined O_3/zeolite and O_3/GAC processes were investigated for the removal of selected pesticides from model water. Five above mentioned pesticides were investigated. Figure 2 shows that in the case of O_3/zeolite combined process were after 0.5 h observed removal efficiencies in the following order: 96.16% HCH, 95.29% HCHBD, 92.60% HCHB and 87.85% PCHB. On the other hand, negligible removal efficiency was achieved for LIN after 0.5 h. After 3.0 h of combined O_3/zeolite process following removal efficiencies were measured: 99.35% HCH, 99.37% HCHBD, 98.36% PCHB and 98.0% HCHB. Only 13.74% removal efficiency of LIN was achieved after 3.0 h of this process.

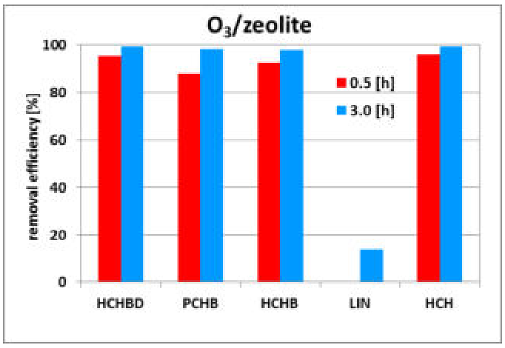

Fig. 2. Removal of pesticides from model wastewater by combined O_3/zeolite process after 0.5 hour and 3.0 hours

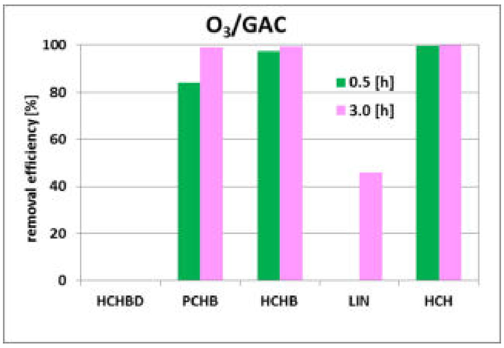

Fig. 3. Removal of pesticides from model wastewater by combined O_3/GAC process after 0.5 hour and 3.0 hours

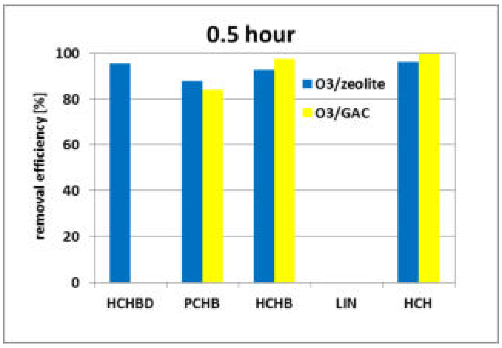

Fig. 4. Removal of pesticides from model wastewater by combined O_3/zeolite and O_3/GAC processes after 0.5 hour

From Figure 3 is obvious that in the case of combined O_3/GAC process were after 0.5 h observed removal efficiencies in the following order: HCH (99.62%), HCHB (97.36%) and PCHB (84.07%). Concentration of HCHBD was lower than the limit of detection also at the beginning of the process. The highest removal efficiencies were achieved after 3.0 h performance of combined O_3/GAC process in the following order: HCH (99.72%), HCHB (99.17%) and PCHB (99.08%). Similarly to previous reaction time the lowest removal efficiency of O_3/GAC process was also after 3.0 h observed for LIN (45.92%). Measured efficiencies were in the case of this process slightly higher than those measured by combined O_3/zeolite process.

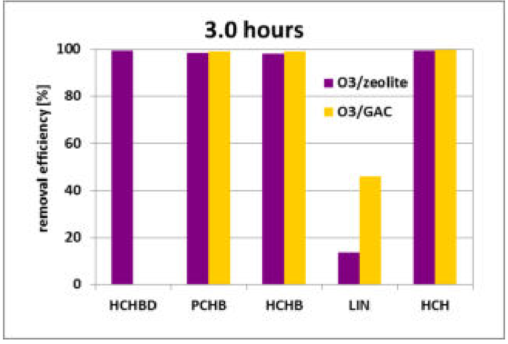

Fig. 5. Removal of pesticides from model wastewater by combined O_3/zeolite and O_3/GAC processes after 3.0 hours

In Figure 4 there are shown the removal efficiencies of pesticides observed for individual pesticides after 0.5 h by both combined processes, i.e. O_3/zeolite and O_3/GAC. Similar comparison of these processes after 3 hours of ozonation time is shown in Figure 5. From these Figures follows that the slightly higher removal efficiencies for majority removal efficiency was measured by O_3/GAC process in the case of LIN. Removal rate of LIN was higher by app. 180% in comparison to O_3/zeolite process. It can be concluded, that both studied processes resulted in very high removal of majority selected organochlorine pesticides excepting LIN. Significantly higher both, the removal rate as well as removal efficiency for LIN were measured when applying O_3/GAC process

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EVALUATION OF ENVIRONMENTAL LOAD – ABANDONED Sb, Au DEPOSIT PEZINOK

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Many projects have dealt with the problems of contamination generated by mining activities in the area between Pezinok and Pernek (Malé Karpaty Mts.). According to the results of these projects the whole area is contaminated and dangerous for human health. Existing data indicate water, soils and stream sediments contamination by arsenic and antimony in the area of Pezinok-Kolársky vrch. Acidification of the environment is significant in the area of abandoned pyrite deposits Čmele and Augustín (Chovan et al., 2006).

GEOLOGY – DEPOSIT SITUATION

There are two types of mineralization present in the area of Pezinok deposits: 1. metamorphosed pyrite-pyrrhotite stratiform mineralization and 2. hydrothermal Sb-Au mineralization. Though occurring separately, both mineralizations are spatially confined to productive black shale horizons of the Pezinok-Pernek crystalline complex (Chovan et al., 1992).

The stratiform pyrite-pyrrhotite mineralization forms concordant, markedly bedded layers, lens- and nest-shaped accumulations, as well as impregnations in metamorphosed host rocks. Parallel ore layers, up to 2 – 3 m thick, recur to form immense ore zones as much as 80 m thick and up to 1 km long. The pyrite ore were mined here from the end of 18th century, the most intensive period took part in the second half of 19th century and mining finished in 1896. In the interval form 1850 – 1896 118 000 tons of pyrite ore were mined for the propose of sulfuric acid production. Examples of deposits: Pezinok (Ferdinand-Karolina), Pernek, Augustín (Chovan et al., 1992).

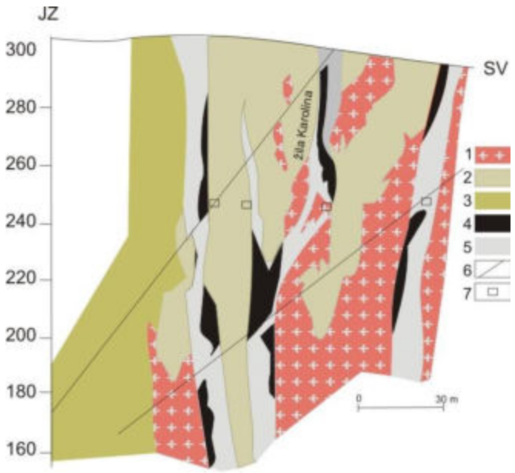

Fig. 1. Geological profile of the Sb-Au deposit Pezinok-Kolársky vrch (modified after Mikula in: Andráš et al., 1999). Legend: 1. granitoides, 2. metamorphic rocks (phyllites, amphibolitic schists, biotitic gneisses), 3. amphibolites, 4. black schists with syngenetic pyrite-pyrrhotite mineralization, 5. epithermal mineralization with quartz lenses, 6. drill holes, 7. adits.

Stibnite and gold-bearing mineralization is confined to formations of black shales embedded in actinolite schists and amphibolites. The mineralization displays a strata-bound character and occurs in form of lenses, quartz-carbonate veinlets, nests and impregnations in the host rocks (**Fig. 1**). The most extensive productive zone in the Pezinok-Kolársky vrch deposit is up to 1 km long, 50-70 m thick; with the vertical extent of 60 – 100 m. Examples of deposits include Pezinok – Kolársky vrch, Trojárová, Staré mesto (Chovan et al., 1992). Stibnite deposit Pezinok-Kolársky vrch was exploited from the beginning of 18th century, while more intensive mining period started in 1906, when flotation plant was built here. The largest amount of ore was exploited in the interval from 1940 to 1992, when the mine was closed.

ENVIRONMENTAL LOAD

Abandoned Sb deposit Pezinok – Kolársky vrch is a significant source of As and Sb pollution that can be traced in the upper horizon of soils several kilometers downstream. Two tailing impoundments which hold ~380 000 m^3 of mining waste and outflows from several adits are the main sources of the metalloids (**Fig. 2**). The tailings and the discharged water have circumneutral pH values (7.0 ± 0.6) because the acidity generated by decomposition of primary sulfides (pyrite, FeS_2; arsenopyrite, FeAsS; stibnite, Sb_2S_3) is rapidly neutralized by abundant carbonates (Majzlan et al., 2007).

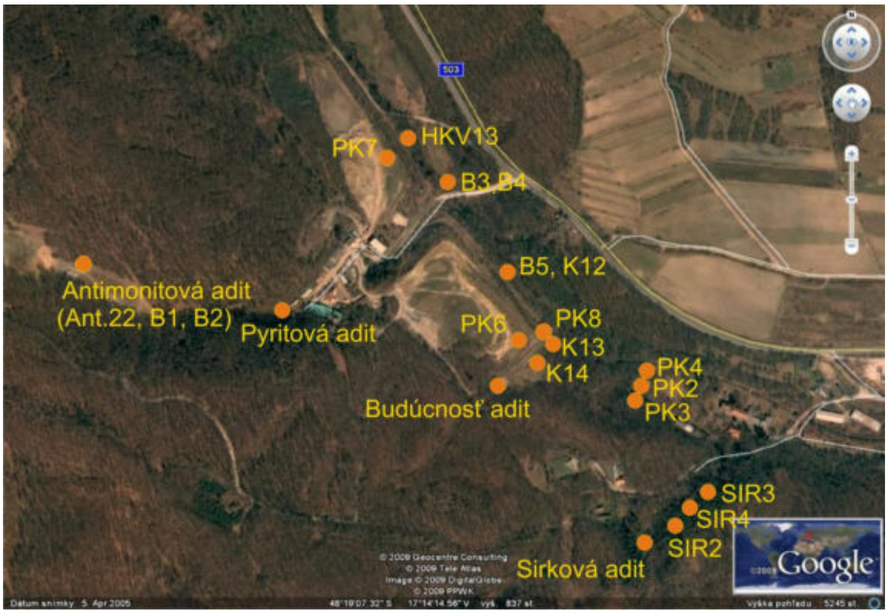

Fig. 2. Schematic map of the abandoned Sb deposit Kolársky vrch, with localization of adits, drill holes and ochre samples sites.

The weathering rims on the primary sulfides are iron oxides which act as very efficient scavengers of As and Sb. Oxidation rims on pyrite obtain up to 10.12 wt.% of As and up to 7.5 wt.% of Sb; As content in rims on arsenopyrite is lower according to unaltered sulfide, conversely Sb content is up to 50 wt.%. In-situ µ-XANES experiments indicate that As in the weathering rims is fully oxidized (As^{5+}). Rims on stibnite were not observed, but there is a large amount of secondary Sb and Sb-Fe oxides present in mine tailings. We suggest that Sb oxides are products of stibnite oxidation and Sb-Fe oxides (including tripuhyite $Fe(II)Sb(V)_2O_6$) has probably crystallized from solutions in the environment of mine tailings (Lalinská, 2009).

Experimental oxidation of sulfides has shown, that stibnite is the most unstable mineral in mine tailings, while pyrite and arsenopyrite are more stable.

We have also investigated mineralogy and chemical composition of ochreous sediments accumulated in the studied area. Samples were collected mainly from mine drainages and also from drill holes in alluvium sediments and mine tailings. Fraction under 0.063 mm was analyzed using conventional methods, including X-ray diffraction, IR spectroscopy and sequential extractions. Schwertmannite was identified as predominant mineral phase in acidic conditions (in outflow of Antimonitová adit), but while carbonates are very common in the studied locality, neutral pH prevails and therefore ferrihydrite is precipitating most often. In older sediments ferrihydrite transforms to more stabile goethite. Total content of As is up to 9152 mg/kg in case of schwertmannite-bearing sample and varies from 433 mg/kg to 130 g/kg in ferrihydrite-bearing samples; Sb content in schwertmannite-bearing is up to 59.8 g/kg and in ferrihydrite-bearing samples is in range from 16.42 mg/kg to 20.3 g/kg (Lalinská 2009).

Samples with ferrihydrite contain Fe and As in their highest oxidation state and in octahedral and tetrahedral coordination, respectively, as suggested by XANES and EXAFS studies on Fe K and As K edges. The iron octahedra in the As-HFO share edges to form short single chains and the chains polymerize by sharing edges or corners with the adjacent units. The arsenate ions attach to the chains in a bidentate–binuclear and monodentate fashion. In addition, hydrogen-bonded complexes may exist to satisfy the bonding requirements of all oxygen atoms in the first coordination sphere of As^{5+} (Majzlan et al., 2007).

Content of dissolved arsenic in subsurface waters is highest in the area of mine tailings (up to 90 mg/l in water sample from drill hole PK7) and arsenic is predominantly pentavalent. Concentration of antimony in this sample is lower – 920 µg/l. Content of arsenic in waters from adits outflows varies from 13 µg/l to 104 µg/l (Pyritová adit), with average content 41 µg/l. Antimony concentration in this kind of samples is conversely higher then that of arsenic and varies from 14 µg/l up to 654 µg/l (Pyritová adit), with average content 196 µg/l (Chovan et al., 2006). Contents of arsenic and antimony in unfiltered water samples are much higher, what means that a high amount of these toxic elements is transported in the form of solid phases. Significant relationship between arsenic and iron suggests sorption of arsenic onto iron oxyhydroxides, however, in case of antimony there are also other mineral phases expected. Fe oxyhydroxides are unstable mineral phases and already a small change in pH and Eh values of the environment could cause desorption of the contaminants. This all means that natural attenuation is not a good system for remediation of the studied area and therefore effectiveness of zero valent iron as appropriate reactive medium for Permeable Reactive Barrier (PRB) was tested (Lalinská, 2009).

Fe^0 - REACTIVE MEDIUM FOR PERMEABLE REACTIVE BARRIER

The choice of Fe^0 as a filling in reactive material for a PRB, was based on publications, which dealt with the suitability of this filling material for arsenic adsorption. While arsenic and antimony are very common elements, we decided to test this filling material also for antimony removal. We have performed 3 batch and 4 column tests to study the usefulness of zero-valent iron for arsenic and antimony removal from contaminated water. In the first stage of experiment, batch tests were run with three different types of iron: iron powder (Lambda), Fe chip (Merck) and steel manufacturing by-products in the form of turnings. All pilot experiments were successful, with the best results observed in case of laboratory Fe chips (100% of antimony removed in 4 hours), but the removal efficiency of much cheaper iron turnings was also suitable (100% of antimony removed in 8 hours). In the second stage we have focused on effectiveness of these materials in column experiments. We used various mixtures of filling material such as: iron powder mixed with sand in ratio 700g of sand/70g of iron powder; 700g of sand/140g of iron powder; pure iron powder in combination with pure sand; steel manufacturing by-products (in the form of turnings) and, finally, turnings mixed with sand. In these experiments we were trying to find out how thick the barrier needs to be able to decontaminate the water, based on the known water velocity. The best results were observed by using iron turnings as the reactive material, where content of As decreased from 22.5 mg/l to 20 µg/l and content of Sb decreased from 4480 µg/l to 29 µg/l (Lalinská, 2009).

Based on the obtained data applied on the model of contaminants transport in the area, two possible designs of PRB were suggested (**Fig. 3**):

1. continual trench (iron filling)
2. funnel and gate (iron filling, separating clay walls)

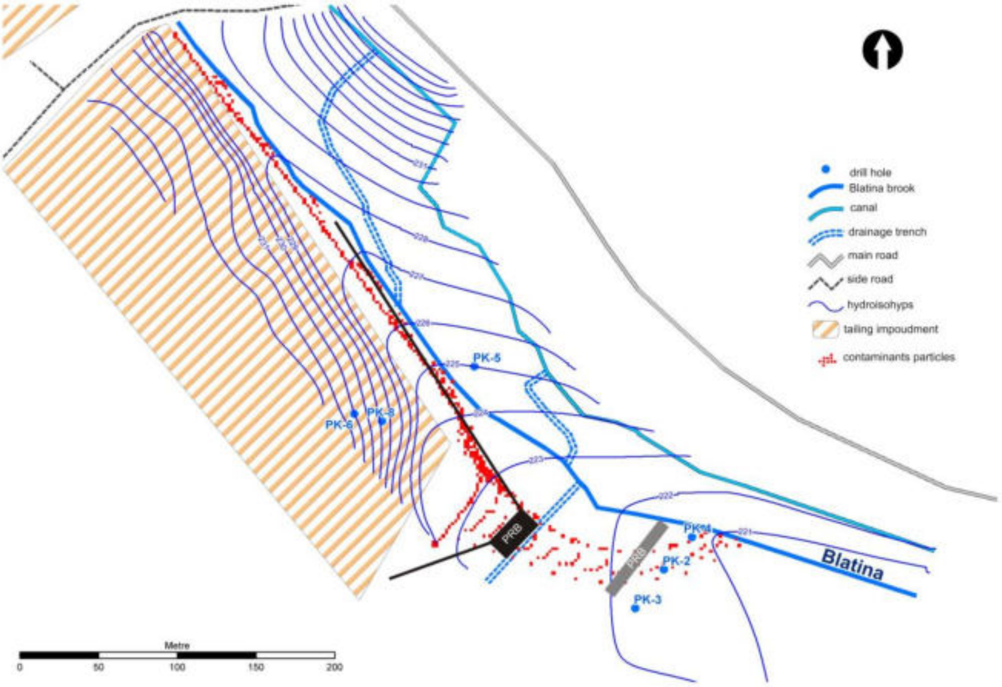

Fig. 3. Model of contaminants flow (minimal water level and unaffected water flow; Krčmář et al., 2007), with localization of two alternative designs of PRB: grey color - continual trench; black color - funnel and gate.

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