INTERNATIONAL CONFERENCE
CONTAMINATED SITES 2016
BRATISLAVA 12–13 SEPTEMBER

INTERNATIONAL CONFERENCE
CONTAMINATED SITES 2016
Bratislava 12 – 13 September 2016

CONFERENCE PROCEEDINGS

MINISTRY OF ENVIRONMENT OF THE SLOVAK REPUBLIC

SK EU2016 Slovak Presidency of the Council of the European Union

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SLOVAK ENVIRONMENT AGENCY

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THE RELEVANCE OF SOILS AND SOIL SCIENCE TOWARDS REALIZATION OF THE UNITED NATIONS SUSTAINABLE DEVELOPMENT GOALS

Luca Montanarella

European Commission, Joint Rewearch Centre, Italy

KEYWORDS
Soil, sustainable development

ABSTRACT

Soil science, as a land-related discipline has important links to several of the SDGs which are demonstrated through the functions of soils and the ecosystem services that are linked to those functions. The following steps are to be taken by the soil science community as a whole: (i) Embrace the UN Sustainable Development Goals, as they provide a platform that allows soil science to demonstrate its relevance for realizing a sustainable society by 2030. (ii) Show the specific value of soil science: Research should explicitly show how using modern soil information can improve the results of inter- and trans-disciplinary studies on SDGs related to food security, water scarcity, climate change, biodiversity loss and health threats. (iii) Given the integrative nature of soils, soil scientists are in a unique position to take leadership in overarching systems-analyses of ecosystems; (iii) Raise awareness of soil organic matter as a key attribute of soils to illustrate its importance for soil functions and ecosystem services; (iv) Improve the transfer of knowledge through knowledge brokers with a soil background; (v) Start at the basis: educational programs are needed at all levels, starting in primary schools, and emphasizing practical, down-to-earth examples; (vi) Facilitate communication with the policy arena by framing research in terms that resonate with politicians in terms of the policy cycle or by considering drivers, pressures and responses affecting impacts of land use change; and finally (vii) all this is only possible if researchers, with soil scientists in the frontlines, look over the hedge towards other disciplines, to the world-at-large and to the policy arena, reaching over to listen first, as a basis for genuine collaboration.

ADDRESSING THE SUSTAINABLE DEVELOPMENT GOALS

The broad Sustainable Development Goals (Table 1) are intended to be a guideline for all governments.Some Goals are mainly socio-economic in character (e.g. Goals 1,4,5,8,9,10,11,16,17) while others focus clearly on the biophysical system, in which soils play a clear role (e.g. Goals 2,3,6,7,12,13,14,15).

It is important to recognize that for most SDGs, there is no direct linkwith soils.Rather, soils contribute to general ecosystem services, defined as “services to society that ecosystems provide” which requirescooperation between different disciplines (e.g. De Groot et al., 2002; Dominati et al., 2014). Ecosystem Servicescontribute to nearly all land-related SDGs, either directly or indirectly. Table1 shows ecosystem services as they are now recognized in the soil literature(e.g.Dominati et al., 2014).The question can be raised as to how input of soil expertise can be most effective when defining ecosystem services. A logical way to consider soil contributions to interdisciplinary studies on ecosystem services is to consider the seven soil functions, as defined by the European Commission (EC, 2006) (Table2). Thus, an operational sequence is defined starting with the SDGs, next considering relevant ecosystem services and the contributions that the soils can make to improve those services (see also Fig. 1). Most applied soil studies can be expressed in terms of their relevance for certainSDGs, also indicatingwhichecosystem services and associated soil functions play an important role.This new possibility for framing soil studies,offers an opportunity to increase the visibility and recognition of the work in soil science as a much wider audience is being addressed.

A clear framework linking SDGs, ecosystem services and soil functions will also pave the way towards a more relevant contribution of the soil science community to on-going major global and regional ecosystems assessments related to land and soils. The most obvious example is the currently on-going Land Degradation and Restoration Assessment (LDRA) of the Intergovernmental Platform for Biodiversity and Ecosystem Services (IPBES), planned for final release in early 2018 (Montanarella, 2015). Similar to IPCC, these assessments by IPBES will be the main scientific reference for future policy development on terrestrial ecosystems at global, regional and national scale.

Overall, we should acknowledgethat services are provided by nature, and that human efforts should be governed by the realisation that every ecosystem has its own, characteristic dynamics and thresholds.Sustainable development can only be achieved when taking into account processes,feedbacks and thresholds in the eco-system.

Tab. 1. The UN "Sustainable Development Goals" for the period 2015–2030. ((http://sustainabledevelopment.un.org/focussdgs.html), related to ecosystem services and soil functions, as discussed.)

	Eco-system services	Provision of food, wood and fibre	Provision of raw materials	Provision of support for human infrastructures	Flood mitigation	Filtering of nutrients and contaminants	Carbon storage and greenhouse gases regulation	Detoxification and the recycling of wastes	Regulation of pests and disease populations	Recreation	Aesthetics	Heritage values	Cultural identity	**Relates to soil function (Table 2)**
SDGs topic		1	2	3	4	5	6	7	8	9	10	11	12	
1	End poverty in all its forms everywhere	X	X	X	X									1,5
2	End hunger, achieve food security and improved nutrition and promote sustainable agriculture	X		X										1,2,4
3	Ensure healthy lives and promote well-being for all at all ages	X							X	X	X	X	X	1,2,3, 4,5,7
4	Ensure inclusive and equitable quality education and promote lifelong learning opportunities for all												X	7
5	Achieve gender equality and empower all women and girls													
6	Ensure availability and sustainable management of water and sanitation for all				X	X		X		X				2
7	Ensure access to affordable, reliable, sustainable and modern energy for all	X	X											1,5,6
8	Promote sustained, inclusive and sustainable economic growth, full and productive employment and decent work for all	X	X	X										1,2,5, 6
9	Build resilient infrastructure, promote inclusive and sustainable industrialization and foster innovation		X	X										2,4,5
10	Reduce inequality within and among countries													
11	Make cities and human settlements inclusive, safe, resilient and sustainable		X	X										2,4,5
12	Ensure sustainable consumption and production patterns	X	X			X	X	X						1,2
13	Take urgent action to combat climate change and its impacts				X		X							2,6
14	Conserve and sustainably use the oceans, seas and marine resources for sustainable development													
15	Protect, restore and promote sustainable use of terrestrial ecosystems, sustainably manage forests, combat desertification, and halt and reverse land degradation and halt biodiversity loss	X	X	X	X	X	X	X	X	X		X	X	1,2,3, 4,5,6
16	Promote peaceful and inclusive societies for sustainable development, provide access to justice for all and build effective, accountable and inclusive institutions at all levels			X						X		X	X	4,7
17	Strengthen the means of implementation and revitalize the global partnership for sustainable development													

Tab. 2. The seven soil Functions (SFs) as defined by the European Commission (EC, 2006)

1	Biomass production, including agriculture and forestry
2	Storing, filtering and transforming nutrients, substances and water
3	Biodiversity pool, such as habitats, species and genes
4	Physical and cultural environment for humans and human activities
5	Source of raw material
6	Acting as carbon pool
7	Archive of geological and archaeological heritage

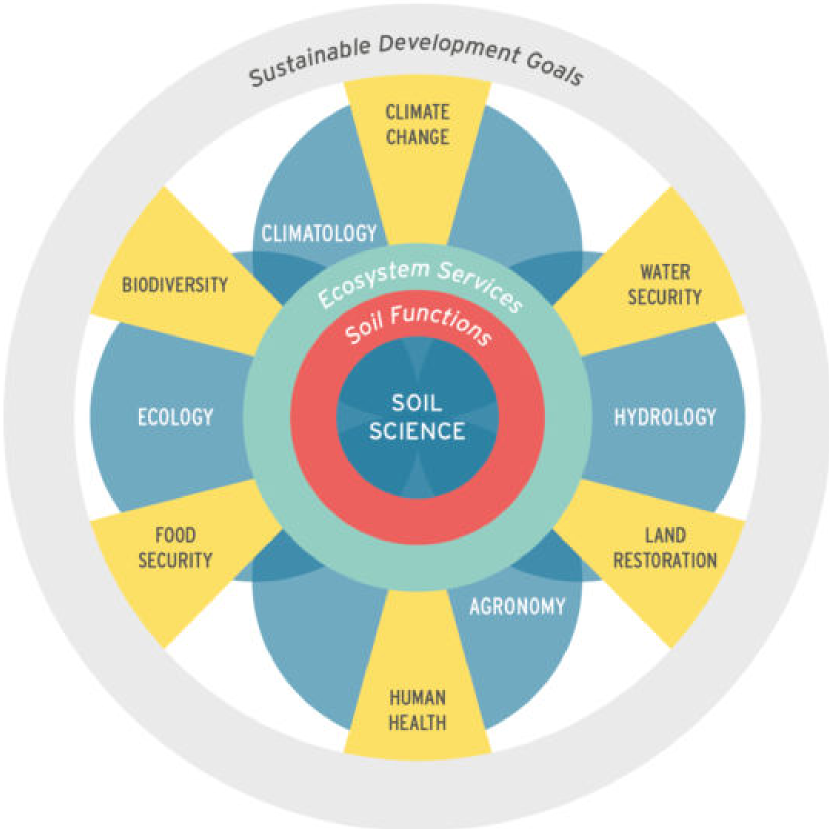

Fig. 1. shows six major global issues, each of which relates to one or more of the SDGs: (i) food security; (ii) human health; (iii) land management, including land restoration; (iv) water security; (v) climate change, and (vi) biodiversity preservation. Source: Keestra et al., 2016.

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STATE OF THE ART IN CONTAMINATED LAND MANAGEMENT – TOWARDS THE 4THGENERATION POLICY FRAMEWORK

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KEYWORDS
soilcontamination, sustainableland management, governance

ABSTRACT

Starting during the1980ies European countries developed contaminated land policies nationally. Through CLARINET a coordinated action funded be the European Commission the common 3rd generation concept has been developed and is still well recognised as Risk Based Land Management. The focus of discussions on the proposal of Union's Soil Framework Directive from 2006 onwards inhibited further evolution in concepts and approaches. However during the same period European policies, perspectives on remedial objectives and integrated solutions in water and land management changed reasonably for not only getting cost-effective solutions but moreover to target resource efficiency and sustainability. The need to meet new challenges calls for discussing how to reframe and develop a policy framework encouraging innovation in contaminated land management.

INTRODUCTION

By 2014 the proposal Draft Soil Framework Directive has been withdrawn. Still it is important to recognise that the European Commission emphasised to *"remain committed to the objective of the protection of soil and will examine options on how to best achieve this" (*OJ C 153 of 21 May 2014).

In order to contribute to a European debate Common Forum on Contaminated Land aims to clarify concepts and map how to make environmental protection, "risks" and "sustainability" complementary in managing contaminated land (the soil-sediment-water-system and its services). Developing common ground for a new frameworkwill also be challenged to address various geographical and time scales, from site to regions at short, medium and long terms.

EVOLUTION OF CONTAMINATED LAND POLICIES

Historically land management was governed by the fact that land and in particular soil is a private property. Like spatial planning schemes alsosoil protection frameworks in Europe started to get developed at national or at regional level. Legislative issues usually were integrated into other sectoral policies and such often started by focussing on agriculture for maintaining fertile soils to grow food and feed.

During the early 80ies of the 20th century environmental scandals due to seriously polluted sites started to receive broad public interest (Ferguson, 1999). Like Lekkerkerk in the Netherlands, a former landfill reused for housing but containing hazardous wastes, several European countries started national programs on site remediation seeking a maximum risk control. These 1st generation policy frameworks also involved systematic approaches for developing national inventories and protocols. Remediation was advised to clean-up sites completely and restore "multifunctional" nearby pristine sites but frequently resulted in high public or private expenditures.

During the 1990ies a 2nd generation of policies developed possibilities for enhancing cost effectiveness by stepwise (tiered) approaches in investigation and risk assessment. Furthermore land use considerations, an improved understanding on fate and transport of contaminants, and exposure assessment in human health risk assessment became more important for preparing decision making.

So far the last and 3rd step in policy framing for Risk Based Land Management (RBLM) was suggested by CLARINET (Vegter, Lowe, Kasamas,Eds.; 2002). Recognising socio-economic development of European societies, increased competition on soil resources and anticipating the relationship between soil and water managementneeds for a better integration with spatial planning became evident. Accordingly CLARINET aimed to go beyond soil protection and turned discussions towards the term *land* as a general spatial concept referring to any geographical area such as a site or a region, and integrating physical components, such as *soil* and *groundwater*beneath the surface of the land. In reframing its management two key features were addressed:

- The time frame and requirements of assessing risks, priorities and long term effects of particular choices
- The choice of solution in assessing overall benefits, costs and environmental side effects, community views and other issues

Considering the three pillars of RBLM (see fig. 1), fitness for use and protection of environment describe the goals in relation to a safe use of land, long-term care allows for flexibility how to achieve these goals.

Fig. 1. The architecture of Risk Based Land Management (Vegter, Lowe, Kasamas, Eds.; 2002)

THE EUROPEAN POLICY FRAMEWORK IN PLACE

The general policy framework at European level has been provided through the Thematic Strategy for Soil Protection[COM(2006)231], which in its origin addressed four lines of action (pillars), namely awareness raising, research, integration into other policies, and legislation. The proposal for a Soil Framework Directive was set out at the same time. However, being a matter of debate for more than 7 years this legislative proposal was withdrawn in 2014(OJ C 153). Nevertheless there remain three lines of action, which have been promoting through various initiatives.

Awareness raising was a particular objective throughout the International Year of Soils in 2015. Integrating soil protection to other policies has been a permanent effort connecting the topic e.g. to industrial installations by adopting the adopted Industrial Emissions Directive (IED, 2010), which improved provisions to ensure that the operation of an installation does not lead to a deterioration in the quality of soil (and groundwater) and introduced an obligatory soil status report as a prerequsite for permitting industrial activities.

Besides legislation also integrated environmental policy like the Roadmap on Resource Efficiency ([COM(2011)571]) and the 7th Environment Action Program (EAP, 2013) kept emphasising soil protection and a communication of the European Commission on landis under preparation.Outlining how Europe's economy shall be transformed into a sustainable one by 2050 and the Roadmap started shifting attention that environment should be understood in terms as being our natural capital providing for ecosystem services and finally economic prosperity. As for*land and soils* the major objective is reducing the rate of land take and achieving no net land take by 2050. The 7th EAP set out 10 priority objectives and underpinned that Europe keeps aiming to protect and the Unions's natural capital as well as to turn into a resource-efficient, green and competitive economy.

Finally being part of European Cohesion Policy around €3.1 billion were allocated in the period 2007-2013 to rehabilitate industrial sites and contaminated land, which meant more than 6 % of planned EU investments under the Environment theme.

NEEDS TO MEET NEW CHALLENGES BY A 4th GENERATION POLICY FRAMEWORK

During the recent years new challenges like climate change, a world-wide financial crisis, shortages of resources and energy, economic recession, migration and new social uprisings became major drivers of policy. As a consequence also the focus of environmental policies is turning again, questions how to balance people, the planet and profit are under debate again and "sustainability" is getting a key-word.
In terms of remediating contaminated land first European documents providing frameworks have already been issued by the UK Sustainable Remediation Forum (SuRF UK, 2010) and the Network on Industrially Contaminated Land in Europe (NICOLE, 2010). In general there is a serious indication for a need of evolution in contaminated land policy framing. At the one hand it means to keep on broadening the integration of risk assessment, spatial planning, soil and water management. On the other hand future decisionshow to manage land need to consider new common policies (e.g. Sustainable use of natural resources; EU climate and energy targets) andwider socio-economic issues. Accordingly risk assessment, investigating and understanding environmental impacts and risks aims to prepare well informed decisions, and land management, which means designing and implementing actions to reduce negative consequences and balance benefits, may strive for improving its sustainability.

Tab. 1. Contaminated Land Management 2020 - complementary concepts for informed decisions and better solutions

	RISK	SUSTAINABILITY
Origin / use	economy/science	ecology/policy
based on	mental construct	ethical construct
Objective	transparency	fairness
Importantelements	o singletarget o accountability o effectiveness	o multi-objective o interdependency o efficiency
Question	Shouldweact?	Howcanweact?
Supports	betterdecisions	betteraction
Strategy	preventorlimit	synergy

WHAT WE NEED TO ENHANCE

Given the background of environmental, economic and societal development and new policy directions future contaminated land management will need to turn its focus from stand-alone site solutions to integrated projects crossing geographical and time scales (site to region to globe; short-, mid- and long-term), which are tailored for matching human needs to natural resources and the capacities of land. Key principles should be to promoting synergies and avoiding irreversibility.Improving governance will be needed and with regard to contaminated land management involves two lines of frames:

- 1st line of governance: improving risk governance to support risk-informed land management at the relevant scale (e.g. municipality, river basin / water catchment, etc.);

- 2nd line of governance: introducing stewardship and project governance to support sustainability of contaminated land remediation and management.

To address future demands and improve ***land management*** towards ***sustainability***innovation in environmental project governance will need to be discussed and convey

- _fairness_ and appropriate consultation processes to facilitate a possible consensus of involved stakeholders,
- _transparency_ of generic policy principles and reasonings as well as site-specifically derived criteria supporting decisions at the project level,
- _efficiency_ in conducting measures and meeting risk reduction goals.

Alongside another line of improvement for conveying more sustainability in the general framework would be to open the discussion on the risk acceptance and tolerability which has a huge impact on the risk calculations prescribed by the regulators to the liable parties.

SUSTAINABILITY IN LAND MANAGEMENT

Referring to the three pillars of sustainability (see fig. 2) it will be crucial to discuss and clarify specified objectives. Environmental sustainability sets out for (i) protecting environment and humans against risks on the long term, (ii) reducing emissions and footprints in land remediation and management and (iii) avoiding a shifting of problems and unacceptable trade offs. Economic sustainability asks for (i) decreasing direct costs amd increasing benefits (decoupling and"factor 4"-projects), (ii) rising property values and (iii) responsible finance mechanims throught a project lifespan. Discussing social sustainability is still a rather new domain in contaminated land management, although it implicitely has already been discussed with regard to brownfields.

Fig. 2. Sustainability – balancing society, environment and economy

Sustainability cannot be quantified in absolute terms. Consequently, stakeholder engagement is crucial to ensure that a sustainability assessment minimises uncertainties in its consideration of project-specific issues and concerns at all stages of remediation (projects (characterisation, planning or project design). This allows stakeholders to provide their perspectives on the balance of potential impacts and benefits. In addition control, or feedback, is integral to informing better land management decisions (Joint Position Paper Common Forum – NICOLE, 2013).

Summarised, our societies and future projects need risk-informed and sustainable solutions for contaminated land management and call for discussions how to develop a 4th generation policy framework.

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THE IMPACT OF EU LEGISLATION, PRINCIPLES AND CASE LAW ON THE NATIONAL CONTAMINATED LAND REGIMES

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KEY WORDS
Contaminated land regimes, baseline report, environmental liability, industrial emission directive, environmental principles

ABSTRACT

A country's Contaminated Land Regime (CLR) is the national regulation applicable to the polluted land and/or groundwater. CLR is one of the few areas of environmental law where detailed legislation is not in place at the EU level.
Despite this, EU environmental law and European Court of Justice (ECJ) case law address matters that are relevant for national CLRs.
First, the Industrial Emissions Directive 2010/75/EU has important implications for the identification of the remediation targets, as it requires the redaction of a Baseline Report. This report needs to describe the state of soil and groundwater at the beginning of the activities, so as to allow for an assessment of the changes occurred, if any, upon their definitive cessation.
Second, the ECJ has generated important case law on the Environmental Liability Directive 2004/35/CE, which indirectly influences the allocation of the remediation costs. Traditionally, such case law posed the whole burden of the remediation on the responsible party only. A 2015 decision has, however, taken a different direction, allowing the States to impose remediating obligations also on site owners which have not caused the pollution.
Given this context, the question this paper aims to address is whether and to what extent national CLRs of the Member States are receptive to the developments in the EU legislation and case law outlined above.

INTRODUCTION

A country's Contaminated Land Regime (CLR) is the national regulation applicable to the land, subsoil and/or groundwater polluted by substances that can cause significant harm to the health of the environment or of organisms living therein. Such regulation usually entails a set of rules aimed at deciding whether the mentioned pollution or significant harm are in place or can reasonably be expected. These legal regimes also define how the remediation targets should be identified, who should pay for the clean-up, and which administrative procedures and monitoring should occur for these purposes.

CLR is one of the few areas of environmental law where detailed legislation is not in place at the EU level. Important policy decisions are thus left to the discretion of the Member States. Arguably, the most important of these decisions concerns the allocation of the burden and costs of remediation. Several CLRs fluctuate between fully adhering to the polluter-pays principle on the one hand, and mitigating it through the stewardship principle on the other. The polluter-pays principle establishes that only the polluter should pay for the remediation. Consequently, if the polluter is not found or is not in the condition to pay, either the remediation is funded by taxpayers or it does not take place. On the contrary, according to the stewardship principle, the landowner – even when not responsible for the contamination – should pay for at least part of the remediation.

Despite the lack of a general European framework on contaminated land law, EU environmental law and ECJ case law regulate and address matters that are relevant for the drafting, interpretation and implementation of national CLRs. Examining this matter might contribute to the development of policy recommendations for the EU soil strategy, with a view to turning economic development and environmental protection into two compatible imperatives.

EU LEGISLATION (DIRECTIVES AND PRINCIPLES)

As for EU legislation, the impact of both EU directives and principles on the national contaminated land regimes should be taken into account.
To this end, the most relevant Directive is the recent Industrial Emissions Directive 2010/75/EU (IED). It introduces a new obligation, namely the redaction of a Baseline Report. In order to ensure that the operation of an installation does not deteriorate the quality of soil and groundwater, the industrial operator is required to produce a Baseline Report describing their state, in order to assess possible changes upon definitive cessation of the activities. The obligation to produce a Baseline Report introduces the duty for the operator of an activity to investigate and disclose the contamination of soil and groundwater, if any. Depending on the features of the specific national CLR, such mandatory disclosure can generate remediation obligations for different parties, which would otherwise have arisen much later, or not at all.How is the Baseline Report obligation established by the IED being implemented by the Member States? According to the IED, an increase in the pollution level triggers the obligation to return the site at least to the state described in the Baseline Report. However, the features of the remediation obligation as a whole are not defined by the IED, but rather left to the discretion of the Member States. What is peculiar here is that the Baseline Report will interfere with the CLRs by requiring the enactment of an administrative procedure uniform at European level. National legislation and guidelines implementing the Baseline Report obligation do not take explicitly into account its inevitable links with the national CLRs[1]. A similar approach was adopted by the European Commission Guidance concerning baseline reports[2]. However, it is likely that the (European) implementation of the Baseline Report will gradually help shape a more consistent (national) CLRs.

Some EU principles are also important to interpret the national CLRs and have been repeatedly invoked to this end. The best known principles that come into consideration are the polluter-pays principle, the stewardship principle, and the precautionary principle. However, also the recently proposed "principle of environmental harm" is likely to assume growing importance, as a key tool aimed at homogenising the interpretation of environmental law. All these principles do not easily converge towards a simple and consistent regulation. While the polluter-pays principle traditionally put the whole burden on the polluter alone, the other mentioned principles (stewardship principle, precautionary principle and principle of environmental harm) do imply a partially different approach. As we will see in the next paragraph, the Courts' interpretation of these principles is playing a decisive role in nudging the national CLRs towards a more uniform approach.

ECJ CASE LAW

As forECJ case law, for the purposes of this paper the most relevant decisions pertain to the Environmental Liability Directive 2004/35/EC (ELD).

Three important 2010 decisions are related to situations where there was an ongoing remediation of a contaminated area that had been polluted by waste dumping (ECJ decisions of 9 March 2010; Cases C-378/08, C-379/08 and C-380/08). Despite the fragmented legal scenario they had to deal with, the 2010 ECJ decisions overall suggested an interpretation of the ELD which pushes the Member States towards a rigid application of the polluter-pays principle in the allocation of responsibility.

A more recent decision has, however, taken a slightly different direction. In 2015, the ECJ has determined that, in circumstances where it is impossible to identify the polluter or to have that person implement the remediation, EU law precludes national legislation from *not* requiring the landowner to take on at least part of the burden of remediation (ECJ of 4 March 2015 – ECJ Case C-534/13). The Court, deciding in relation to the Italian CLR, concluded as follows:

"*Directive 2004/35/EC … on environmental liability must be interpreted as not precluding national legislation … which, in cases where it is impossible to identify the polluter of a plot of land or to have that person adopt*

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[1] For instance, in Italy, according to art. 242 of Legislative Decree no. 152/2006, the obligation to undertake the remediation arises as result of the exceeding of certain risk threshold values (CSR). Remediation obligations in relation with the Baseline Report, instead, depend on whether there has been a deterioration of soil and groundwater due to the industrial activity.

[2] Commission, *"Communication from the Commission — European Commission Guidance concerning baseline reports under Article 22(2) of Directive 2010/75/EU on industrial emissions",* COM 2014/C136/03.

remedial measures, does not permit the competent authority to require the owner of the land (who is not responsible for the pollution) to adopt preventive and remedial measures, that person being required merely to reimburse the costs relating to the measures undertaken by the competent authority within the limit of the market value of the site, determined after those measures have been carried out".

Contrary to its previous tendency to support a rigid interpretation of the polluter-pays principle (insistently advocated also in the Opinion of the Advocate General Kokott), with this decision the ECJ gives new strength to the stewardship principle. Although the decision allows national CLRs not to force the 'innocent' landowner to directly and fully implement the remediation, it does imply a minimum standard of obligation for the landowner in cases where it is impossible to have the remediation implemented by the polluter. In such situations, the decision implies that the ELD must be now interpreted as providing national CLRs with a choice between the following two options only:

a) requiring the 'innocent' landowner to adopt full preventive and remedial measures,

or, at the very least,

b) requiring the 'innocent' landowner to reimburse the costs related to the measures undertaken by the competent authority up to the limit of the market value of the site following the remediation.

In both cases, the burden imposed on the landowner is rather heavy, as an application of the stewardship principle (as well as of the precautionary principle and of the principle of environmental harm) would require.

CONCLUSIONS

Three main conclusions emerge from this brief analysis.

First, in Europe the national CLRs will probably be receptive to the developments in the EU legislation and case law outlined above. This might even lead, at least in some member states, to a common, although 'unofficial', EU CLR, based on some common principles and a shared language. The standardization process will probably focus on the following provisional list of points:

i. how the CLR defines the system to be used in order to classify a land as contaminated (whether according to a set of limit thresholds or a case by case risk analysis);
ii. how the CLR identifies the liable party (polluter; present and 'innocent' landowner; past 'innocent' landowner(s); operator of the activity);
iii. what criteria the CLR establishes for dealing with contaminated areas where nobody voluntarily takes up the responsibility for the remediation;
iv. what tools the CLR puts in place to identify the remediation targets, for both soil and groundwater.

Second, despite an initial reliance on the polluter-pays principle alone, recent developments in the EU case law have given increased prominence to the stewardship principle. Hence, despite not explicitly regulating contaminated land, legislation and case law at the EU level have the potential to nudge the national CLRs towards mitigating the polluter-pays through the stewardship principle. Interestingly, some CLRs contain rules which differentiate the public from the private law domain, particularly in the crucial area of the allocation of the remediation costs. In the former, the stewardship principle seems to prevail, whereas the latter is dominated by the polluter-pays principle.

Third, contrary to what common knowledge of environmental liability might suggest, both the ELD and the recent ECJ case law extend the application of remediation rules to three - rather than two - different parties. Apart from the polluter and the 'innocent' landowner, the ELD also refers to the operator, defined by Art. 2(6) as

"*any natural or legal, private or public person who operates or controls the occupational activity or, where this is provided for in national legislation, to whom decisive economic power over the technical functioning of such an activity has been delegated, including the holder of a permit or authorisation for such an activity or the person registering or notifying such an activity.*"

According to this definition (which is very similar to the definition of 'operator' provided by art. 3 of the IED), the operator does not necessarily coincide with either the polluter or the 'innocent' landowner. It would be very interesting to analyse the operator's legal obligations as they emerge from this legislation and case law and are being interpreted by the national CLRs.

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A NEW NATIONAL RISK ASSESSMENT FRAMEWORK FOR CONTAMINATED SITES IN AUSTRIA – LAND-USE-SPECIFIC EVALUATION OF SOIL POLLUTION AT HISTORICALLY CONTAMINATED SITES AND OLD LANDFILLS

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KEYWORDS
Austrian Standard,soil contamination, site remediation, land use, risk assessment, toxicological derived values

ABSTRACT

The Austrian Standard ÖNORM S 2088-2 “Contaminated Sites – Part 2: land-use-specific evaluation of soil pollution at historically contaminated sites and old landfills” is part of technical guidance in its 2nd generation which was adopted by 1. September 2014. Technical approaches within the respective framework were supposed to reflect state-of-the-art approaches in Europe, but should respect and meet expectations of practitioners for pragmatic solutions as well. This is felt to be crucial for the acceptance of new concepts towards a new legal framework for historically contaminated sites. ÖNORM S 2088-2 is intended to provide fundamentals (i) to evaluate results from field investigations and (ii) to perform a simplified initial (first tier) risk assessment in order to identify or exclude possible chronic effects on human health originating from soil pollution. With regard to the exposure pathway “soil-human” a classification of 5 different land uses is suggested: playground (oral ingestion scenario), residential use (inhalative scenario), agricultural and horticultural use (inhalative scenario), recreational use (no predefined scenario) and industry, commerce and infrastructure (no predefined scenario). With regard to land use classes characterized by predefinedreference scenarios soil screening values are provided. Additionally, ÖNORM S 2088-2 includes 4 Annexes providing for complementary information. Annex B summarizes details (including data justifying exposure parameters) how soil screening values have been derived mathematically.

BACKGROUND

In Austria remediation of contaminated sites refers to several laws (e.g. Water Act, Waste Management Act) which were, at the time of origin, not intended for managing historical contamination, but aiming at integrated environmental protection and therefore refer to the precautionary principle. Up to now no national “Soil Protection Act” exists, however some provinces have “Soil Protection Acts” in place. Under the “Contaminated Sites Remediation Act” (ALSAG; enacted 1989) taxes on waste are raised with the objective to finance and fund remediation of seriously contaminated sites.
The Austrian Standard ÖNORM S 2088-2 (issued 2000) was the first to describe a general protocol and generic criteria like trigger and intervention values for contaminated soil. These screening values can be regarded as conservative. By 2011 Environment Agency Austria published the first technical guidance document (Reichenauer et al., 2011) on site-specific human health risk assessment (HHRA) for contaminated sites. In consequence it became also necessary to revise the general protocol provided through ÖNORM S 2088-2 and to debate the aim and derivation processes fortrigger values.

THE DISCUSSION PROCESS

Alreadyin 2008 a shift in environmental policy for historically contaminated sites was discussed. As a resultthe Austrian Environment Ministry published a policy paper defining new key objectives for contaminated site management by 2009. In consequencerisk assessment needed to turn towards a site- and land use specific approach.. In 2011 Environment Agency Austria established its guidance on “Exposure assessment and risk analyses for contaminated sites” (Reichenauer, T. et al.; 2011). Complementary a revision of the Austrian Standard ÖNORM S 2088-2became necessary.In adapting the standard towardsland-use specific risk evaluation for contaminated soil,its trigger values were derivedwith reference to generic exposure scenarios and indicate a negligible intensity of soil contamination, which can be regarded as “generally acceptable risk”.

Duringthe period from 2009 until 2013 relevant stakeholder groups were involved to the discussion process for identifying relevantland use classes, exposureparameters and scenarios forsettingtrigger values.At the beginning of the discussion process 4 land use classes (living, residential use, agriculture and industry) were agreed. However, later on a fifth land use class (playground) was added. This was less due to a technical rationale, but simply mirrors a generally high societal sensitivity, which asks for preventing and minimizing contaminant exposure of children.

LAND USE CLASSIFICATION

In characterizing and evaluating soil contamination and impacts on human health and ecosystems (fig. 1) all data and knowledge of the site need to be used for describing a holistic Conceptual Site Model.As well several chemical and physical processes like adsorption, absorption, dispersion, diffusion and degradation influence the distribution, accumulation and finally contaminant exposure.

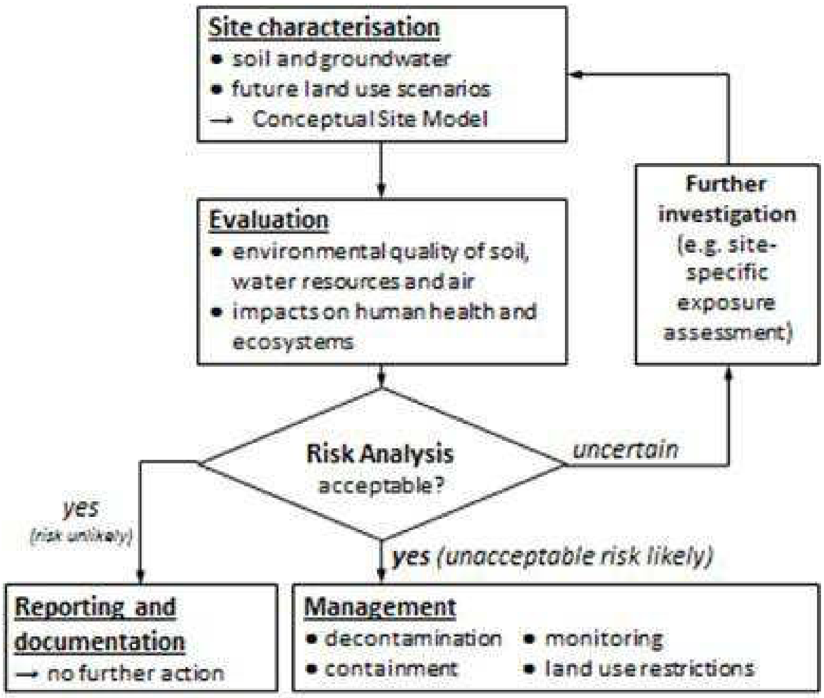

Fig. 1. contaminated sites – characterisation and evaluation of soil contamination and impacts on human health and ecosystems.

The Austrian Standard ÖNORM S 2088-2 in its 1st edition 2000 had established trigger and intervention values for a generic assessment on oral contaminant exposure only. Furthermore this had been focused to playgrounds and residential areas, although aspects on contaminant uptake by plants were included as well. In difference the 2nd edition of the standard sets out for different land-use classes and for a prescribed generic risk appraisal characterized by land-use specific reference scenarios.
Finally land use classes are additionally characterized by typical activities (e.g. indoor inhalation, gardening, agricultural work), with each having a different set and combination of exposure pathways, which control oral, inhalative or dermal contaminant exposure.

ESTABLISHING GENERIC EXPOSURE SCENARIOS

In line with the policypaper published by 2009 and with respect to its key objective for site- and land-use-specific risk assessment, it became necessary to revise the entire concept of the standard and to characterize land-use-specific reference scenarios.As a first result of expert to stakeholder discussion some general assumptions were agreed:

- It was decided not to use modelling approaches and complex scenarios combining different exposure pathways, but to derive land-use-specific trigger values according to a sensitivity test for identifying a most relevant activity and exposure pathway.

- To recognize exposure by multiple contaminant sources the additional contaminant exposure by soil contamination is limited by 20 % of the acceptable daily intake (ASI).
- The process of deriving trigger values needsto be transparent and reproducible by a documentation of any alogarithm or exposure parameter.
- Accordingly referring to new scientific data any knowledge based amendment for the generic reference scenarios is feasiblein using the standard on the mid-term.

With regard to the land-use class "playground" the exposure pathway "oral soil ingestion" by children wasconsidered dominant, whereaswith respectto the scenarios "residential use" and "agricultural use" inhalation of dust proofed most sensitive.Finally for a few organic contaminants (dioxins and benz(a)pyren) dermal uptake was considered crucial and most sensitive.

DEFINING EXPOSURE PARAMETERS

In characterizing generic reference scenarios biometric parameters are defined by national statistical data and the choice of sensitive data (e.g. 5% percentile for body weight) reflects a conservative approach. As for time budgets, which are defined by the frequency of an activity and its duration of exposure, no robust references could be identified. Therefore it was a matter of expert to stakeholder discussion to establish exposure parameters (e.g. 90 days a year that a child plays at a playground). Any other exposure parameters like substance ingestion rates or soil-plant transfer rates are referenced by recognized sources and robust scientific literature. Toxicological reference values were chosen from renowned international organizations like the WHO.

Defining exposure parameters for reference scenarios brought about that the user group and annual time budgets for 2 land use classes (residential and agricultural use) were equal. Combined to the predefined assumption that inhalation of dust had been identified being the most sensitive exposure pathway,the results in calculating trigger values for both land use classes were identical (see table 1, column 2).

PLAUSIBILITY TESTING

As a follow-up in establishing generic reference scenarios and defining exposure parameters, trigger values were calculated and the results finally became a matter of expert discussion and plausibility testing considering

- a control and comparison against background values (national data on agricultural and urban soils),
- trigger values from other European countries (Carlon C., (ed.); 2007)
- complementary national legislative documents (e.g. BAWP; "Federal waste management plan", 2011),
- bioavailability data, and
- data on carcinogenic potentials for different metals species.

In general for the most parameters the results of trigger value calculation were confirmed. For a few parameters (e.g. As) plausibility testing and expert discussions resulted in decisions for adapting trigger values.

CONTAMINANT MIXTURES

As organic contaminants like PAH or PCB in practice often are represented and expressed by a sum of reference substances, trigger values were simply defined according to a review of already existing trigger values defined by national or European documents. In particular with respect to TPH (total petroleum hydrocarbons) the trigger valuefor "playgrounds" (see table 1) wasneither derived toxicologically nor referenced to other existing trigger values, but simply represents the intention that society is interested and willing to provide for not only a safe but a clean environment for children.

Tab. 1. Trigger values according toÖNORM S 2088-2:2014 – comparative summary (tables 1, 2 and 3)

Parameter	Dimension	Trigger value		
		playground	residential*	agriculture**
Antimony	mg/kg	5	60	2
Arsenic	mg/kg	20	50	20
Lead	mg/kg	100	500	100
Cadmium	mg/kg	2	2	0,5

Parameter	Dimension	Trigger value		
		playground	residential*	agriculture**
Chromium	mg/kg	100	75	100
Cobalt	mg/kg	-	-	50
Copper	mg/kg	100	500	100
Molybdenum	mg/kg	-	-	2,5
Nickel	mg/kg	70	-	100
Mercury	mg/kg	1	10	0,5
Selenium	mg/kg	-	-	1
Thallium	mg/kg	-	-	1
Vanadium	mg/kg	-	-	100
Zinc	mg/kg	-	-	300
Fluoride	mg/kg	-	-	200
Cyanide	mg/kg	5	-	5
TPH	mg/kg	50	-	200
PCDD/F	ng TE/kg	50	600	10
PCB	mg/kg	0,2	2	0,1
PAH	mg/kg	4	10	2
Benz(a)pyren	mg/kg	0,1	0,5	-

* residential (e.g gardening) or agricultural use: site-specific risk analysis
** further investigation of contaminant uptake by plant
TPH … Total Petroleum Hydrocarbons
PCDD/F … dioxins and furans
PAH … polycyclic aromatic hydrocarbons (16 reference substances)
PCB … polychlorinated biphenyls (7 reference substances)

In general trigger values regarding the land-use class “playground” reflect low risk acceptabilityand stringent limitation of contaminants. Hence as for the parameter chromium in comparison the land use class “residential use” provides for a lower trigger value. Background is the fact that human health is more sensitive against chromium exposure via the exposure pathway “inhalation”than by oral ingestion.
In comparing trigger values provided in table 1it needs also to be recognized that the third column includes trigger values for limiting contaminant uptake by plants in agricultural production.

INDUSTRIAL AND RECREATIONAL LAND USE

Discussions regarding reference scenarios and defining exposure parameters for industrial and recreational land use indicated, that several exposure parameters are likely to show a high variation (e.g. dust depending surface conditions, climate and activities). Furthermore reference scenarios and exposure parameters defined in an iterative process according to the results of expert to stakeholder discussions resultedin trigger values, which generally would have allowed for comparably high intensities of contamination. Due to the fact, that it had not been possible to characterize consistent reference scenarios the expert discussion resulted in a decision, that a derivation and tables of generic trigger values for industrial and recreational land uses would not be appropriate. However ÖNORM S 2088-2provides by its appendix C some basic information how to characterize exposure scenario site-specifically.

MANAGING SOIL QUALITY – A SAFE OR A BETTER PLACE?

How clean is clean? This question cannot be answered by a standard. As there is no simple answer it needs an open stakeholder dialogue for establishing effective soil management procedures and guidance documents. Moreover acceptance by involved stakeholders is vital. In contaminated land management standards or guidance documents should providescientific and technical knowledge ready for informing all interested parties.

The revised 2nd edition of ÖNORM S 2088-2 allows for different levels of contamination with respect to land use. This fact indicates that general acceptance of risk-informed decision is growing.However not only playgrounds for children butany residential use of land likely involves a high personal interest of owners and residents. Citizens usually not only want a “safe” place (without serious risks) but a “good” place worth living to. Whereas site-specific exposure assessment and risk analysis may help to limit contamination for a “safe” place, ÖNORM S 2088-2 aims on good soil quality and introducing its trigger values as target values for site remediation will as well support creating abetter place, without use restrictions or long-term maintenance efforts.

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RISK ASSESSMENT IN WALLONIA (BELGIUM): THE GOOD AGREEMENT BETWEEN LIMIT VALUES AND DETAILED RISK ASSESSMENT THE RISK ASSESSMENT: A TOOL TO DECREASE THE REMEDIATION COST - EXAMPLES FROM SPAQUE

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KEYWORDS
Risk assessment, toxicology, sustainable remediation, screening values, limit values, tiered approach

ABSTRACT

The risk assessment occupies a special place in soil legislation enforced in Wallonia since 2008. It has to be a useful tool to help in decision-making to answer the questions: does the soil quality match with the current or the future land-use? If remediation works are required, what levels of clean-up need to be reached?
SPAQuE, in charge of many abandoned polluted sites, has proposed a tiered-approach risk assessment methodology, offering flexibility, rapidity or/and accuracy, depending on the environmental situation. This methodology, described in the Good Practice Guide, consists of 3 levels of risk assessment, from aneasycomparison with screening values to an actual site-specific assessment. Then, examples of remediation costs calculated for several polluted sites supported by SPAQuE are shown. At last, someimprovement points in the risk assessment field are presented, explaining that risk assessment cannot be considered as a frozen framework but improves thanks to new scientific data, keeping in mind a sustainable remediation.

INTRODUCTION: ROLE OF SPAQUE AND SOIL LEGISLATION IN WALLONIA

SPAQUE is in charge of remediation of abandoned polluted sites in Wallonia, the French-speaking part of Belgium, in order to return the land to economical activities. Thanks to European and regional funds, SPAQuE is able to follow the remediation of 50 sites. From 2001 to 2016, 24 sites - 602 ha - were cleaned up. SPAQuE was also in charge of developing the risk assessment methodology for the Walloon Government, for the Soil Decree implementation. As abandoned sites are often very contaminated over a very large area, the risk assessment methodology had to be easy to use on one handbut avoiding over-estimatedremediation coston the other hand.

Soil legislation in Wallonia was enforcedthrough the Soil Decree passed in December 2008. After soil and groundwater investigations, remediation works can be implemented, depending on the risk assessmentresults. In Wallonia, the risk assessment follows a tiered approach, with increasing complexity:

1) The screening assessment using trigger values developed on a risk-based methodology, called also generic guideline values or limit values;
2) The Tier 1 risk assessment;
3) The Tier 2 or detailed risk assessment.

MATERIAL AND METHOD: THE METHODOLOGY TO CALCULATE THE TRIGGER VALUES

The trigger values were calculated by SPAQUE in 2007-2008 for the Walloon Government, following the risk assessment methodology defined by the National Research Council, in USA (**NRC, 1983**),in the reverse mode, using conservative assumptions. Three trigger values, equal to the maximum acceptable concentrations in soil, were established for the protection of 3 kinds of receptors: the human health (called VS_H), the aquifers (called VS_N) and the terrestrial ecosystems (called VS_E). The selected trigger value which becomes the screening value is the lower value. A trigger value, similar to drinking-water quality, was also calculated as maximum concentration in groundwater.

The trigger values for human health protection were calculated byCSOIL equations **(RIVM, 1996**) available in RISC-HUMAN model (Van Hall Instituut, the Netherlands).Theprocedure for the risk assessment for human

health consists of comparing potential exposure levels on the site occupants are exposed to those levels where no toxic effects are expected to occur.
The trigger values for groundwater protection were calculated by equations adjusted on Connor model (**Connor, 1997)** to evaluate leaching and dispersionof soil pollutant into groundwater.
The trigger values for ecologicalprotection werebased onexisting ecotoxicological data from available specific literature.

Trigger values were calculated for 5 land-uses: natural, agricultural, residential, park/commercial and industrial and for 50 pollutants: metals, BTEX, PAH (Polycyclic Aromatic Hydrocarbons), mineral oil, chlorinated solvents and cyanides.

Since 2015, the Walloon government has been replacing RISC-HUMAN model by S-RISK model (**VITO, 2015**), recently developed by VITO (Flanders, other part of Belgium) in order to harmonize the soil legislation in the 3 regions of the Country (Wallonia, Flanders, Brussels).

After the trigger values are calculated and before becoming "screening values", an important step must not be forgotten: are the trigger values reachable and detectable? The proposed trigger values must be compared to the background levels (for metals for example) andto analytical limits of detection (LOD).

RESULTS AND DISCUSSION: THE RISK ASSESSMENT IN 3 STEPS

First, soil and groundwater concentrations measured on site are compared to trigger values. If trigger values are not exceeded, the risk assessment stops, concluding that "risks are acceptable", the "soil quality is compatible with the current or future land-use" and no remediation is required. No land-use restriction is needed either.
Otherwise, if trigger values are exceeded, the assessor can go to the Tier 1 risk assessment or directly to the Tier 2 risk assessment.

In the Tier 1 risk assessment, soil and groundwater concentrations measured on site are separately compared to VS_H, VS_N and VS_Etrigger values, in orderto define the receptors for which the risk is unacceptable, and keeping in mind that most of the time, the lowest trigger value is the ecological value (VS_E).
In the Tier 2 risk assessment, some site-specific information is used as input data in the exposure model. The following usual parameters are modified: depth of contamination, exposure duration, exposure route, organic matter content, soil texture (sand, silt, clay), building dimensions, etc.
In this last step, information about the development project is necessary. All the site-specific data can lead to land-use restrictions such as no removalof soil, no drinking-water well, no garden with vegetables, etc.In Belgium, the land-use restrictions are noted in a "soil certificate", to preserve the environmental history of the site.

The 2 first levels of risk assessment(screening level and Tier 1) have the advantages of rapidity, ease and don't need to use models. In the case of remediation works, the clean-up levels in soil and groundwater aredeveloped with very conservative assumptions and could lead to an expensive cost.

The Tier 2 risk assessment has the advantages of using site-specific data in order to obtain a more sustainable remediation cost. However, the use of exposure models needs special skills and takes more time before getting the answer.In the case of remediation works, the clean-up levels in soil and groundwater are developed taking into account risk assessment results and remediation technologies.

RESULTS AND DISCUSSION: INTEREST OF RISK ASSESSMENT FOR THE SUSTAINABLE REMEDIATION OF CONTAMINATED SITES

In the following table, the estimated (and not true)remediation costsdepending on the risk assessment level are described and the remediation project selected by SPAQuE is coloured in red.

The table 1 shows different environmental situations and explains that the choice of the risk assessment level depends on the site characteristics.

Tab. 1. Estimation of remediation cost for different contaminated sites supported by SPAQUE (the selected alternative chosen by SPAQUE in red) –costs in millions Euros

Clean-up level	VS ❶	VS_H (tier 1) ❷	Site-specific (tier 2) ❸	Price gap
Chimeuse - zone 4 (9 ha)	22,9		11,8	- 48 %
Boch Kéramis (17 ha)	12,7		4,8	- 62 %
Cristalleries VSL (5,2 ha)	9,1	6,5	1,7	- 82 %
CAM Comblain la Tour (3 ha)	2,6		0,4	- 84 %
Ancienne Base Wing Tactique (59 ha)	0,89	0,68		- 24 %

PERSPECTIVES: RECENT SCIENTIFIC INFORMATION IN THE RISK ASSESSMENT FIELD

A lot of input parameters are usually proposed by default in the exposure models. Replacing the default values by more recent values, particularly for influencing parameters, can lead to a more realistic risk assessment.

For exposure assessment, the soil ingestion rate established by VITO (**VITO, 2008**) – 63 mg/d and 87 mg/d for adults and children respectively –or recently by EPA (**US-EPA, 2011**) could be used instead of old typical EPA values– 100 mg/d and 200 mg/d. This parameter has a high influence for metals and PAH assessment.

For toxicity assessment, the selection of the most appropriate reference values and not the most protective values could help to decrease the remediation cost. Care must be taken with the necessary updating of toxicity reference values as these could significantly modify the results (example: new EFSA toxicity value for lead (**EFSA, 2010**)). For exposure assessment, bioaccessibility data – if available - could be taken into account in order to be more representative of the "real" exposure. The bioaccessibility rate, usually fixed to 100 %,is defined as the fraction of contaminant that can be available from soil to be absorbed during gastro-intestinal digestion. For example, bioaccessibility data was used by SPAQuE for a large-scale risk assessment of pollution in private gardens near industrial activities (**SPAQuE, 2015**).

For exposure assessment, the assess or rarely has measurement data on indoor air or on vegetables because the site is often a brownfield site without existing buildings or gardens. The soil/air transfer and the soil/plant transfer are estimated by models and have high influence for volatile pollutants and "residential with garden" land-use respectively.

For exposure assessment, some exposure models propose exposure pathways linked todermal exposure and permeation phenomena (passage of the contaminant in soil through a buried and porous water distribution pipe leading to contamination of drinking water). Based on equations containing high uncertainties and a lack of specific toxicity data for dermal contact, questions about both relevance and accuracy of these exposure pathways can be asked and could be studied again to become more reliable.

These points mentioned above explain that risk assessment cannot be considered as a frozen frameworkbut is constantly improving thanks to new scientific data.

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LESSONS LEARNED AFTER 20 YEARS OF SOIL REMEDIATION POLICY IN FLANDERS

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KEYWORDS
Soil remediation, policy, Flanders, transfer of land, soil certificate, soil investigation, use of excavated soil, risk assessment

INTRODUCTION

In 1995, Flemish soil remediation was boosted by the Soil Remediation Decree. In this decree tactical choices were made leading to a number of new legal instruments:

- a difference between historical and new contamination was made: it gives a signal to pay attention to pollution prevention, on the other hand flexibility was guaranteed to treat the old problems;
- a difference was made between obligation to remediate and liability;
- an economical driving force is linked to soil remediation: land transfer. Soil quality becomes an element of real estate price;
- a duty for local authorities to develop an inventory of risksites was installed. A risksite is a parcel of land where an activity has or had an elevated risk for soil contamination.

In 2006 the Flemish government decided to adapt a new contaminated land decree. The novelty of this decree consisted in the fitting of soil remediation with the plans for land management by the individual owner.Prevent new contamination and remediate historical contamination are the main objectives of the Decree for soil remediation and soil protection from 27th October 2006, ratified by the Flemish government.

After 20 years of soil remediation policy Flanders has learned that most of the instruments were successful for the planned purpose, namely the remediation of the historical contaminated land in a period of 40 years. Some instruments proved to be ineffective while others needed an adjustment. Finally, new policies need to be installed in the coming years. The presentation will give an overview of the lessons learned.

SOIL INVESTIGATION

There is an obligation of investigation of soils at the moment of property transfer, on a periodical base or by closure of certain installations who can or could cause soil contamination.The authorities may also gather information as a result of its investigations into soil quality. The exploratory investigations include a limited investigation into the past history of the soil, as well as restricted sampling operations.

If these investigations indicate the presence of contaminating substances, the need for further soil investigation depends on comparison of the concentrations with soil remediation values. During a descriptive soil investigation the contamination will be characterized in detail and the risk for humans and ecosystems will be defined. The aim of this investigation is to give a description of the nature, quantity, concentration and origin of the contaminating substances, the possibility that these might spread, and the danger that human beings, plants and animals, as well as surface and groundwater, might be exposed to the contaminating substances.

After 20 years of experience the OVAM has learned that good procedures for soil investigation are necessary to have a level playing field. The ordering party has to know what kind of efforts are demanded in his specific situation. Local situations can be very divers, so procedures have to describe clearly what is required. A clear linkage of the different investigation steps is necessary to save costs.

NEED FOR REMEDIAL OPERATIONS

There is made a distinction in policy depending on the origin of the soil contamination. "Historical" soil contamination is contamination originated before the first Decree came into force; this is before 29th October 1995. "New" soil contamination originates after the Decree came into force.

The remediation of new pollution is, according to the Decree, required as soon as the soil remediation values are exceeded. With respect to historical contamination, the decision to remediate will depend on the actual danger to man and the environment (non quantified general criteria). So a risk-assessment approach is followed in the descriptive soil investigation. The remediation actions are determined in a soil remediation project. The Public Flemish Waste Agency (OVAM) supervises the remediation operations.

LAND INFORMATION REGISTER (LIR)

The Land information register is an inventory of all the parcels of which data are known at the OVAM. The LIR serves as a data base for policy decisions and also functions as an instrument to protect and inform potential buyers of contaminated sites.The GIR is open to the public. The soil certificate, an extract of this register for a specified ground, gives all the information known by the OVAM. The maintenance of the register requires a lot of work but the retribution that is asked for the soil certificate brings the OVAM more than 10 million euro a year.

OBLIGATION FOR REMEDIATION AND LIABILITY

In the Flemish Soil Decree a remediation obligation rests on the operator, the user or the owner of the land where the pollution entered the soil. This means also that the obligation does not rest on the owner of the land contaminated by migration of contaminating substances from another property. If new contamination is concerned, the obligation exists automatically. In the case of historical contamination, the obligation only arises after the remediation order by the government.

The Flemish Soil Decree introduced a non-retroactive strict liability rule and channeled the liability for the new contamination to those that caused the contamination. Recourse against other responsible parties is however possible. With respect to historical contamination, liability is determined by the rules in effect before the decree came into force.

The user or operator of the land where the pollution entered the soil is not obliged to carry out the remediation if he can prove that he did not cause the contamination himself (by his fault or otherwise) and that the contamination did not come to existence in the period of the use of the land. The owner needs to prove that next to these requirements he was not and should not have been aware of the pollutionwhen acquiring the property. In addition is the owner for historical contamination not obliged to carry out the remediation if he proves that the contaminated land was acquired prior to 1993 and was since then exclusively used for a non-professional use although he had prior knowledge of the pollution.

The legislation with the obligation to remediate has proved to be a strong instrument to realize effective remediation works. The polluter of historical contamination is very often difficult to find. The system of exemption of the obligation has to be worked out well to keep the burden for the owners socially acceptable and fair.

EXECUTION

The various steps in the soil remediation procedure need to be carried out under the direction of an independent soil expert accredited by the OVAM, the so-called soil remediation expert. This expert must for the execution of his tasks follow the standard procedures and codes of good practice as established by the OVAM. Likewise, sampling and analyses must be carried out by an accredited agency.

The exploratory soil investigation examines whether there are serious indications of soil contamination on a given site. This involves a limited historical examination and limited sample-taking.The exploratory soil investigation will be conducted:

- on the initiative and at the charge of the transferor, before the transfer of lands at risk. These are sites on which a facility is or was established or where an activity is being or was carried out that is included in the list of potentially contaminating activities;

- on the initiative and at the charge of the operator, before the closure of a facility or the cessation of an activity on the 'list';
- on the initiative of the operator before a certain date, and, thereafter, periodically, for some categories of activities or facilities that are included in the 'list'.

The OVAM may, at any time, conduct an ex officio exploratory soil investigation. The OVAM can also send an investigation order to an owner if there are indications of a serious contamination.

After 20 years of experience we know that some land with historical riskactivities is not investigated through this kind of obligations. So Flanders is preparing an adjustment of the soil decree, so that the owners of that land will have to execute an exploratory investigation before 2025. To guarantee the quality of all soil investigations and remediation works a system of independent and accredited soil experts proved to be very helpful.

SOIL REMEDIATION PROJECT

The soil remediation project, drawn up by the soil remediation expert, establishes the manner in which the soil remediation works are to be carried out. In this process, consideration is given to the best available technical solutions that already have been successfully tested out in practice and whose price is not unreasonable in proportion to the achievable result in terms of protecting people and the environment (the BATNEEC principle).

Remediation of new contaminated soil is in the first place geared to the broadest realization of target values regarding soil quality. Depending on the actual situation and characteristics that are specific to the site, it may in some well-defined instances not be possible to realize the target value by application of techniques that do not result in excessive costs. In these cases, soil remediation is oriented towards the realization of a better quality than has been defined by the soil remediation standards or, if this also is not possible, to the avoidance that the soil quality should constitute a risk or could or might constitute a risk for people and the environment. For historical contamination the aim of the remediation is to remove the risk for human and the environment.
For soil remediation projects, a special procedure based on input and advice has been established, taking into account the special nature of soil remediation projects and the fact that, in general, soil remediation projects are established in the public interest, and that their execution must not needlessly be delayed by an accumulation of administrative procedures.

In this respect, the involved owners and users are advised by the OVAM of the submission of a soil remediation project. They have the opportunity to check out the soil remediation project at the OVAM and at the municipal offices and are given the opportunity to raise objections and remarks. If the needed soil remediation works are subject to a permit, expert advice is also obtained from other competent administrations and local authorities.

On the basis of the assessment of the soil remediation project, the recommendations, objections and/or remarks and comments received, the OVAM will issue a conformance certificate or request additional information on the submitted soil remediation project. This conformance certificate serves as a permit for the planned execution of the soil remediation works.

SOIL REMEDIATION WORKS

Following the declaration of conformity by the OVAM of the submitted soil remediation project, the remediation works can be started. Soil pollution can be remediated via different remediation techniques or a combination of such techniques. These remediation techniques may include the removal or elimination of the contamination or remain restricted to isolating and immobilizing it. Although the removal of the pollutants is in many instances the most efficient solution, this may in certain instances not prove the most advisable method (unacceptable risk factors, extremely high costs vis-à-vis other remediation techniques, ...).

The results of the soil remediation works must be reported to the OVAM in a final evaluation report. On the basis of this final assessment report, the OVAM can deliver a final declaration, in which the results of the soil decontamination are listed. If further follow-up measures are deemed necessary, these will be imposed accordingly in the said final declaration.

TRANSFER OF LAND

Before concluding an agreement regarding the transfer of land, the transferor must request a soil certificate from the OVAM.By transfer of land is meant, amongst others:

- the transfer inter vivos of the property title;
- the assumption or termination;
- the merger of legal persons, at least one of which will be owner of the land;
- the splitting of a legal person who is owner of the land.

In the event of a transfer of land on which an activity is or was carried out or a facility is or was established that is included in the 'list', it will also be necessary to conduct an exploratory soil investigation in advance of the transfer.
In the event that the exploratory soil investigation indicates that a descriptive soil investigation is called for, the OVAM will inform the transferor that such a descriptive soil investigation is needed.If from the descriptive soil investigation it appears that a soil remediation project needs to be instituted, the transfer may only take place on condition that the transferor:

- has drawn up a soil remediation project in conformity with the legislation;
- has committed himself vis-à-vis the OVAM to carry out soil remediation works;
- has posted financial securities.

All of the above-mentioned obligations may likewise be assumed by the buyer of the land or by a party with legal title to proceed to the execution of transfer.

The obligation to give guarantees about the soil remediation as a result of a transfer of land has proved to be a powerful instrument in the Flemish soil policy. An economical driving force has been linked to soil remediation. Soil quality has become an important element of real estate price.

RISK ASSESSMENT

The methodology for site specific risk assessment is based on the approach followed to derive soil remediation standards. A generic approach is followed for the derivation of soil remediation standards, while for site-specific risk assessments certain parameters, such as soil properties, can be adjusted.

Soil remediation standards are based on the protection of human health and on the protection of the ecosystem. Critical values for concentration in the soil are calculated based on human toxicology and others based on ecotoxicology. The most critical value is retained as soil remediation standard.Soil remediation standards for groundwater represent drinking water quality.

THE USE OF EXCAVATED SOIL

During construction projects, road works, installation of utility cables and similar operations, volumes of soil are excavated or stripped from the surface. Sometimes this excavated soil is re-used as filling material on the excavation site. In most cases, however, the excavated soil will be carried off for re-use on other locations. Soil can be re-used for instance for raising the profile of a terrain or filling of pits.

If groundworks are carried out on a contaminated site, chances are very real that existing soil contamination will be spread in this way. In order to prevent this dispersion of soil contamination and to offer sufficient legal security to the different actors involved in the use of excavated soil, the Flemish government drew up directives related to the use of excavated soil. In order to meet the predefined targets, the regulations on the use of excavated soil first impose a soil quality survey. The nature of the excavation works and the volume of soil that is released by them will determine the type of exploratory strategy that has to be followed. Secondly, the regulations fixe the conditions for the use of the excavated soil. Depending on the soil quality, the site for re-use and the anticipated application, the excavated soil can under certain conditions be re-used in-situ or elsewhere. The basic principle here is the stand-still principle, which means that no deterioration of the current environmental condition is allowed. Finally, a tracking procedure guarantees the administrative follow-up of the active soil flows.

The OVAM is acting as the supervising authority in the regulation on the use of excavated soil. The administrative follow-up of the active soil flows is carried out by different organizations (soil management organizations, interim storage facilities and centres for soil purification) that have been accredited by the OVAM.

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MANAGEMENT OF CRUDE OIL AND HEAVY METAL CONTAMINATED SITES IN RUSSIA USING A RISK ASSESSMENT APPROACH

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

ABSTRACT

Federal reports indicate that petroleum hydrocarbons (usually in the form of crude oil) and *heavy metals* are the most frequent soil *contaminants* in Russia. Oil spillage from producing wells, storage tanks and damaged pipelines impacts negatively to ecosystems and human health. Crude oil constituents, e.g. BTEX, PAH, phenols, are highly toxic and carcinogenic. Also heavy metals presented in crude oil and drilling fluid can be accumulated by plants, thus leading to toxic reactions along the food chain. Our research is directed to provide the site-specific risk assessment and to improve response actions to terrestrial oil spills under cold climate conditions. 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 and heavy metals under various soil and hydrological scenarios. Based on risk assessment results, target pollutant concentrations in soil were determined to be achieved during remediation actions. Selected bioremediation strategies were tested at field pilot scale, including bioaugmentation with hydrocarbon-oxidizing metal-accumulating 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]. 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 [2]. 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. The present paper describes a risk based approach to the management and bioremediation of crude oil contaminated site under cold climate conditions in the Perm region of Russia (Fig. 1).

Fig. 1. Oil-contaminated site in the Perm oilfiefd region, Urals, 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]. Among oilfield waste constituents, polycyclic aromatic hydrocarbons, phenols, heavy metals, and radioactive elements are of particular environmental concern. In particular, heavy metals presented in crude oil and drilling fluid can be accumulated by plants, thus leading to toxic reactions along the food chain. 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.

2. RESULTS

A conceptual model 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. We have developed a risk assessment module system "Ecological Risk" for hydrocarbon contamination (RF State Registration No. 2012618687), which realizes multimedia, multipathway and multireceptor approach and can be used for the land management and remediation purposes (Fig. 2).

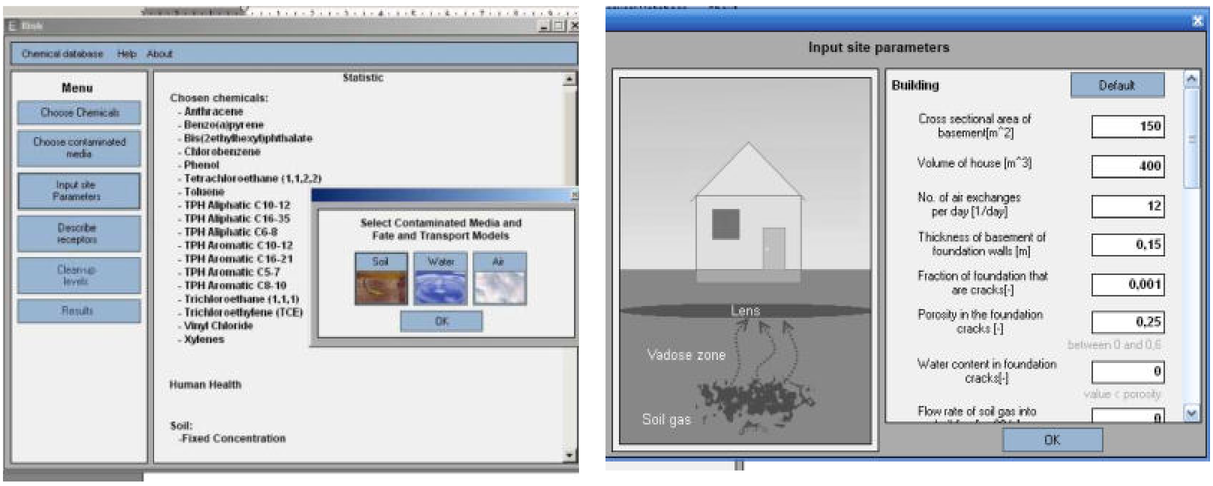

Fig. 2. Risk assessment program for oil-contaminated site evaluations.

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. 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. 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. 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 1.8×10^{-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.

After the site localization, the most suitable remediation method was chosen based on cleanup levels calculated. 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 [10]. The technological scheme developed for highly contaminated (up to 20-30 % wt. of total petroleum hydrocarbons) soil bioremediation involves construction of composting/landfarming cells; preliminary treatment of soil in a biological slurry reactor; phytoremediation of residual contamination by sowing a mixture of perennial grass. To shorten the bioremediation period, the preliminary treatment of contaminated soil in a bioreactor with enhanced ventilation is proposed that allows to decrease remediation time by 2-3 weeks and to achieve maximum oil degradation rate (4-6 % per day). It should be noted that a bioreactor allows both to monitor operating parameters such as temperature, pH, aeration rate, biofrtilizer consumption, microbial biomass density and to use a bioreactor under cold conditions. The resulting bioreactor product, containing residual oil contamination, is loaded into landfarming or composting cells for further decontamination. To enhance bioremediation, different treatments (*e.g.* soil tilling, bulking with woodchips or sawdust, watering and biofertilizer addition) are recommended. Tertiary soil management involves phytoremediation where landfarming/composting cells are seeded with a mixture of perennial grass. Phytoremediation allows rehabilitatation of natural soil fertility and recovering soil quality for further agricultural use.

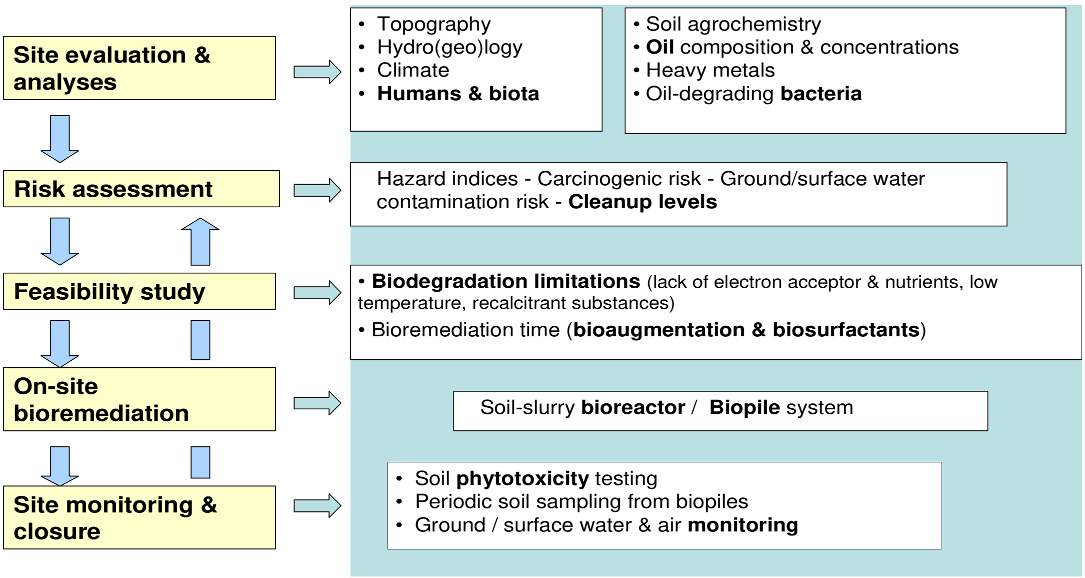

Fig. 3. Flow diagram of risk based management of crude oil-contaminated sites.

Results of the field trial confirmed the effectiveness of augmenting a biopile with the sawdust-immobilized biocatalyst and biosurfactant. 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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Fig. 4. Oil-contaminated site before (*left*) and after (*right*) remediation.

LITERATURE

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DEVELOPING COUNTRIES PERSPECTIVE TOWARDS SUSTAINABILITY IN SITE CLEANUP

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KEYWORDS
Developing countries, contaminated site management strategy, sustainability

ABSTRACT

Despite the economic and social problems most developing countries are facing, the need for a proper strategy related to contaminated site management is urgent. Rather than adapting other countries strategies or implementing general remediation approaches, the strategy should be developed with a tailor-madeperspective in corporating short and long-term goals. Strategic objectives might change from sector to sector (small and medium size denterprises (SMEs) vs. Large enterprises), and might be highly site specific. However, considering recent developments, contaminated site management strategies should be based on a more sustainable rather than traditional approach. As the principles of sustainable remediation has been determined, practical framework sand reference materials (methods, tools etc.) been published, the integration of sustainable practices into the decision-making process is more easy. The sustainable approach in contaminated site management considers a balance between environmental, economic and social aspects. However, regarding the challenges of developing countries with prioritised economic goals, environmental and social benefits of cleanups cannot be threshold or balancing criteria. Slight modifications related to the balance of sustainability principles might help to overcome the obstacles related to the management of contaminated sites resulting from SMEs. Thus, a tailor-made approach might be more practical than the business-as-usual approach for a more sustainable implementation of contaminated site management strategy in developing countries.

INTRODUCTION

The outcome of economic development was and is an increased cumulative environmental impact. The lack of required budged for infrastructure and management programs causes to a delay in the implementation of available precautions and thus in more severe environmental impacts. As both ground and surface water resources are influenced by soil pollution, the need for a contaminated site management program will eventually emerge. A contaminated site program should consider elements of prevention, clean-up, response to and remediation of emergency incidents in order to have a holistic approach to the issue and prevent future contamination (Kovalick and Montgomery, 2014). Currently many developing countries suffer from mismanagement because they lack legislative provisions, enforcement mechanisms and/or budgets.So, the first task is to develop legislation on brownsfields and contaminated sites that further on needs to be supported by a management framework and soil quality standard system. However, countries that have legal instruments, the ambiguity of liability and lack of accountability in relation with the poor management capacity of the authority prolong the development and/or implementation of a contaminated site management program. Therefore, a clear liability system that assigns responsibility for mitigation measures and site clean-up regarding all sectors (public, commercial and industrial sectors) is essential. What is actually more crucial is to have a fund created for the management of contaminated sites requiring complex, systematic and long-term effort. This paper aims to put an emphasis on the problems of developing countries in implementing comprehensive contaminated site management action plans.

CONTAMINATED SITE EVALUATION APPROACHES

The evaluation of contaminated sites may be carried out by using different approaches that are tailored according to national/local needs. While some countries might chose to develop health based standards (indicator, intervention, target values) regarding the intended use of land, some other countries might prefer to use a risk based approach (human health risk or ecological risk). In either case the legislative background of country has to support the contaminated site management system relying on multiple legislations or a direct special legislation. Current practices show a shift towards the human health risk based approach as cleaning up of the site, even to levels needed for future use, might not be necessary if there is no exposure pathway and thus

no risk. So, to avoid unnecessary expenditure of time and money, it would be a wise strategy to use a tiered approach (NICOLE, 2002). Additionally, each country decides on the level of reducing future liabilities by setting the right requirements/constrains with respect to unacceptable risks regarding national/local conditions.
As significant progress has been made in evaluating the fate of contaminants and their possible risk on human health and the environment, different approaches may be developed during the remediation decision making stage. During the prioritisation of contaminated sites, time scales for the remediation and cleanup of contaminated sites might be set for different risk levels. As in the Swiss approach the remedial option, whether containment or clean-up, can be determined with respect to duration of risk(SAGTA, 2008).Accordingly, the duration of remediation project can be selected for different timescales, 10 years, 1 generation (20 or 30 years), 100 years. Within this scope the null model approach, which relies on no intervention (natural attenuation) might be taking into consideration as well. Especially in countries with low budgets, legislations shall allow certain room to manoeuvre in balancing environmental impacts of remediation, remediation costs and quality requirements for natural resources (SAGTA, 2008).

INTEGRATING SUSTAINABILITY INTO RISK BASED LAND MANAGEMENT

The conventional approach in soil remediation, which was based on the effectiveness of the remedy, implementability, cost considerations (capital and operating) and time constraints, does not evaluate and balance fully the external environmental, social and economic impacts of a project (Fiorenza et al., 2009). Tremendous efforts have been given to underspin the application of sustainability principles not only to land management but also to the management of contaminated sites (SAGTA, 2008; Bardos, 2010). While the debate on the implementation on sustainable remediation indicators continues, it is generally accepted that the sustainability principles are applied to all stages of the remediation process – from initial investigation throughout site closure (SURF, 2016).

The development of a guidance document will enable the integration of sustainability into site remediation and to its acceptance by all stakeholders. Additionally, as current approaches and qualitative and quantitative metrics of sustainable remediation are compared and evaluated within time, the implementation of sustainability criteria to each countries interest will be much easier. The development of ISO/DIS 18504 Standard Guidance on Sustainable Remediation in near future will enable regulators to promulgate meaningful rules and guidance to incorporate sustainability into remediation process. The integration of sustainability criteria at the evaluation, design and assessment steps of the remedial action stage of relevant legislative framework is possible. Timescale might be different for each developing country but regarding the development in contaminated site management, it would be wise to integrate sustainability criteria into the human based contaminated site management system. Therefore, developing countries with no current legislation might develop their legislative framework on both aspects. On the other hand, sustainability might be a parallel consideration at more than one stage in those countries that already have adopted or started implementing a human based risk approach.

Within the three pillars of sustainability, the18 indicator categories that have been determined for remediation, indicate to the issues that may be relevant and need to be evaluated during contaminated site management (Table 1). As the creation of funds will not be easy in most developing countries, the incorporation of all criteria might not be possible. However, those countries who already have enforcement and implementation on issues like air and water pollution, waste management, occupational health and safety and incentives on renewable energy and climate changeetc can integrate some of the environmental, economic and social metrics into various stages of contaminated land management. Possible metrics are summarised in Table 2. Examples of sustainability integration schemes to contaminated site management systems have been presented in publications of meetings and conferences (Wisconsin Dept. of Natural Resources, 2012; Thomas and Oakeshott, 2014).

Tab. 1. Headline indicator categories (SURF, 2009)

Environmental	Economic	Social
1. Impacts on air 2. Impacts on water 3. Impacts on soil 4. Impacts on ecology 5. Intrusiveness 6. Resource use and waste	1. Direct costs and direct economic benefits 2. Indirect costs and indirect economic benefits 3. Gearing 4. Employment/human capital 5.Life-span and “project risks” 6. Flexibility	1. Community involvement and community satisfaction 2. Human health 3. Ethical and equity considerations 4. Impacts on neighbourhoods or regions 5. Fit with planning and policy strategies and initiatives 6. Uncertainty and evidence

Tab. 2. Summary of possible metrics

Environmental	Economic	Social
➢ Greenhouse gas emissions (CO_2e) ➢ Energy use and efficiency ➢ Energy source (renewable, natural gas, other) ➢ Water use and reuse ➢ Waste generation, recycling and reuse ➢ Land, material use ➢ Biodiversity (species count)	➢ Capital cost ➢ Operation and maintenance cost ➢ Employment/human capital ➢ Safety costs ➢ Liability discharge ➢ Increase in site/local land/ property values	➢ Transparency and involvement of community ➢ Occupational/community health and safety legislative issues ➢ Impacts and benefits to local areas ➢ Land reuse ➢ Jobs created ➢ Liabilityvs.responsibility issues

MAJOR CHALLENGES OF DEVELOPING COUNTRIES

Developing a national management system for contaminated sites is urgent for many developing countries. A good national contaminated site management system, on the other side requires a well established framework that coordinates policy, regulatory, planning and practice issues. Tremendous efforts have been given to fill in the gaps in contaminated site management especially within the last decade and these experiences are shared by various countries with networks like Common Forum, Sustainable Remediation Forum, NICOLE etc. However, it is still difficult to establish and implement a contaminated site management system, either through the lack of legislative provisions, enforcement mechanisms and/or national budgets. Remediation of contaminated sites will most probably encounter resistance from business managers especially due to liability discharges, high direct and indirect costs involved in remedial actions. As large sale enterprises mostly have the necessary infrastructure to implement other environmental legislations they will soon understand the requirements and start acting. However, medium and smaller scale enterprises still struggle with basic issues like hazardous waste management. So, their encouragement will be long term. On the other side, lack of know-how, national budget and poor management capacity of the authority might also lead to a postponement of the implementation of the contaminated site management plan or enforcement of relevant legislations with all of their articles.

In the early 2020s' the integration of sustainability criteria into a risk based management system will not be avoidable in most developing countries that have the capability of managing air and water pollution, hazardous and solid wastes. Sustainability seeks for a balance between environmental, economic and social impacts during remediation activities. However, if the implementation of sustainability criteria is not performed to the ideal balance but rather to a tailor made level then resistance from the industrial and public sectors may fall. Slight modifications related to the balance of sustainability principles might help to overcome some of the obstacles (Figure 1). These modifications shall be carried out by taking country-specific conditions into account. As economic development is usually of primary importance, emphasis may be second most paid on environmental impacts and less to socialimpacts in general.

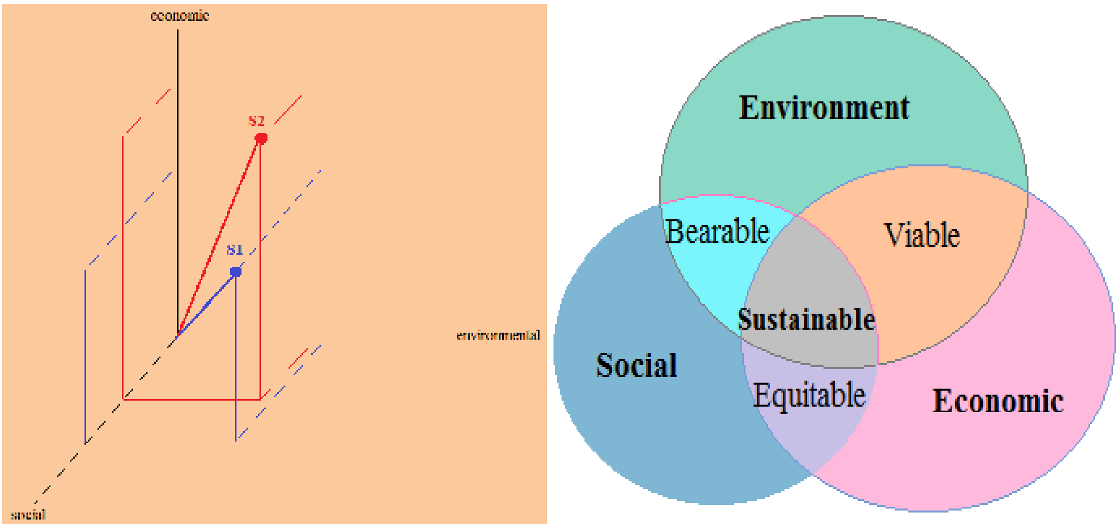

Fig. 1. Schematic presentation of the modified sustainable remediation concept for developing countries.

Forraising awareness on the consequences of not taking measures or postponing the enforcement of relevant legislations, tremendous efforts have to be given to all sectors. It has to be explained to the authorities, consulting agencies and all other stakeholders that not taking measures is the worst choice if there is a human health risk at the contaminated site. Additionally, the approach of European stakeholders that will take part in remedial action within contaminated site management in developing countries shall be supportive, by explaining that cost efficient sustainable remedial action options are available in reducing human based risk at various contaminated sites.

CONCLUSION

Most developing countries have recognised the contaminated site specific problems for human healt hand the environment. The qualitative and quantitative change in water resources in the future with respect to climate change will result in more stress and consequently more economic burden without the implementation of a contaminated site management system. Human based risk assessment is an essential tool in contaminated site management. It provides a structured and transparent approach for sound decision making. By setting the right requirements /constraints with respect to unacceptable risks, country specific conditions can be integrated to the risk based contaminated site management system. The incorporation of sustainability criteria is also recommended to get further into the direction of sustainable resource (soil and water) management. A tiered approach will definitely support a more stable establishment of the management system, by helping to overcome problems related to fund raising and other economic burdens related to remedial actions.

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EVALUATION AND REMEDIATION STRATEGY FOR OIL CONTAMINATED SAND IN KUWAIT OIL LAKE

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ABSTRACT

During the occupation of Kuwait by Iraq in 1990/1991, Iraq's armed forces destroyed more than 700 oil wells. The resulting oil flowed out and formed a large number of oil lakes. This also led to the contamination of soil, which has been left untreated in the deserts of Kuwait for more than two decades now. The untreated contaminated soil has the tendency to pollute the underground watercourses as well as affecting the ecology and humans health. Soil remediation has traditionally been regarded as an afterthought by major oil producers. With increased global environmental standards and the proven ability to use suggested technology (Soil washing method) in the harshest environments with the Kuwait oil sand. Currently one of only 17 pre-qualified companies eligible to bid for the clean-up work. Pre- qualification is a demanding, investigative process between international companies and Kuwait Oil Company (KOC); a success that few companies around the world have achieved. During the multi-year process with KOC, companies are expected to provide five years of historical financial records and up to ten years of technological performance. Soil washing method, which is the suggested method, is expected to make it a frontrunner in the pursuit of future contracts. Furthermore, the soil washing technologies have several strong advantages over competing thermal and bioremediation technologies. These advantages include cost effectiveness and scalability, as well as its unique ability to remove oil residues from contaminated sites for resale in the future. Overall objectives of this project aimed to reduce the concentrations of contaminates to satisfactory levels, which is a subject that has yet to be investigated. This kind of work is vital for successfully meeting the remediation objective, with a system being chosen that offers cost effectiveness, feasibility and short time.

1. INTRODUCTION

The State of Kuwait sustained significant and widespread environmental damage resulting from the Iraqi invasion in August 1990. During the 1991 Gulf War, estimates of 798 oil wells were set ablaze, 149 damaged and 45 gushing oil (Petroleum Economist 1992; Petroleum Energy Center (PEC), 1999). Several oil lakes, i.e., oil accumulation in depressions, were formed. Approximately 12 billion gallons of seawater, which contained substantial amount of salt was used to extinguish around 20 to 25 million barrels of ignited crude oil. The gushing oil and fallout from the oil fire plumes spread over the desert surface covering vast areas stretching from Kuwait to the Kingdom of Saudi Arabia. Within the vicinity of the oil wells, oil deposits were formed with various sizes of lakes and films or oil crust spreading across areas same distance away from the wells. As a result, contaminations of soil and groundwater took place due to oil spray and combustion products from oil fires (Al-Awadhi *et al.,* 1996). The spilled oil which accumulated in low lying areas within Kuwait desert, created more than 300 large oil lakes. These spots comprise a combination of water (28 % average), salt (in excess of 10 %), oil and sand known as "oil lakes" spread over the surface of land. Among these lakes, 45 major lakes were in Burqan and between Maqwa and Ahmadi oil fields. There were another 23 minor lakes (Al-Ajmi *et al.,* 1994; Kwarteng 1998). It is fortunate that the Kuwait Oil Company (KOC) has succeeded in recovering around 21 million barrels from the oil lakes since the end of the Gulf War. The spilled oil was recovered by pumping from the oil lakes to the oil gathering center, then exported as untreated oil (KOC, 2015).This huge scale of contamination has created environmental issues to the ground, air, coast and ground water. Also, the depth of these formed oil lakes vary from a few centimetres to a few metres, which constitute more than 60 million barrels of crude oil. Altogether, around 660 million barrels of crude oil were released to the environment and as a result, approximately 55 million tons of contaminated soil remained in the lakebeds. The existence of such a phenomenal amount of oil over a substantial land area represents a main environmental concern. No other petroleum catastrophe in history came near to equalling the extent of this event (Al-Ajmi *et al.,* 1994; Kwarteng, 1998). As time goes by, low number of benzene ring structure of polycyclic aromatic hydrocarbons (PAH) has been evaporated on exposure to high temperature. The fine soot particles in the form of oil mist became hard while smaller and shallower oil lakes became dry thus forming tarmats.

2.1 SOIL SAMPLING

This project has been focused on the contaminated layer below the oil sludge layer, meanwhile the sludge is taken by the KOC. This showing a major source for future research, but outside the scope of this project. Three different samples have been given by Kuwait National Petroleum Company (KNPC) which were classified as high contamination (45,000 mg/kg), medium contamination (25,000 mg/kg) and low contamination (18,000 mg/kg).

2.2 ANALYSIS OF CONTAMINATED SOILS

During this project, total petroleum hydrocarbons (TPHs) have been found that their concentration levels are greater than the allowable discharge levels in oil contaminated sand. Therefore, it is a requirement to remove these compounds from these contaminated sand by using suitable treatment methods. National Unit for Environmental Research and Services (NUERS), Faculty of Science, Kuwait University, carried out the test for the concentration of TPH in the oil contaminated sand based on (Environmental Protection Agency (EPA) Method 3546, as Hexane Extractable Material).

2.3 REMEDIATION METHOD

The System and the method for remediation of oil contaminated sand (OCS) provides for washing and separation of sand and oil based contamination. As illustrated in Figure 1, the system for for remediation of oil contaminated sand includes feed sieve (FS) 1 for receiving a volume of oil contaminated sand. 200 kg f oil contaminated sand is fed to the feed sieve by a solid pump (SP), and the flow into the soil washing system (SWS) (3) may be selectively controlled by a valve (2). Preferably, the feed sieve 1 is provided with a small size of sieve mesh (10 mm) for separating out large particles (on the order of 10 mm in diameter or greater), such as coarse aggregate (CA), metal pieces (MP), etc. The feed sieve is in communication with a soil washing system (SWS) 3 for receiving the volume of contaminated sand (CS). The soil solution ratio can be about 1:1.5 (mass/volume). After or during the mixing, the volume of oil contaminated sand and water in the washing tank of SWS 3 are able to create a mixture of washed sand and oily wastewater. The overall washing time of approximately 2 hours.It should be understood that the cleaning tank 3 formed from suitable material which will not degrade under the cleaning process such as stainless steel. The SWS 3 is in communication with a sand separator system (SSS) 4 for receiving the mixture. The SSS 4 has an open upper end and an outlet formed in sidewall thereof, the mixture of washed sand and oily wastewater is transported to the SSS to separate out the treated sand (TS), which may then be collected. The separated oily wastewater is pumped to the flocculation tank (FT) 6 using dewatering pump (DP) 5. The washed sand should have an oil residue volume of less than 1% and, thus, may be collected and shipped for the desired purpose thereof. The Washed sand can be used, for example the production of asphalt concrete mixes in road base, secondary roads, impermeable layers for landfills and enhancement of resistance to the penetration of water, chloride ions and the like in concrete, etc.For treatment of oily wastewater, FT 6 is in communication with the outlet of SSS 4 for receiving oily wastewater, FT 6 is used to mix the oily wastewater with at least one coagulant for separation of the oily wastewater into treated water and an oily sludge. It should be understood that any suitable coagulant may be used. For example, approximately 0.5 kg of aluminum sulfate (Alum) in approximately 10 litres of distilled water may be used as the coagulant. Mixing of the coagulant and the oily wastewater in the FT 6 preferably occurs with an agitation speed of approximately 50 rpm for a period of approximately 45 minutes to ensure that the wastewater and coagulant are well mixed. The mixing speed may then be gradually reduced to 0 rpm, followed by a 2 hours settling period. The treated water may then be drawn off and stored in treated water tank (TWT) 8 for reuse again in the system since the oil reside is settled and transmitted using sludge hopper (SH) 7. The oily sludge (accumulation of asphaltenes and resins) may then be collected by for disposal or recycling thereof (9).

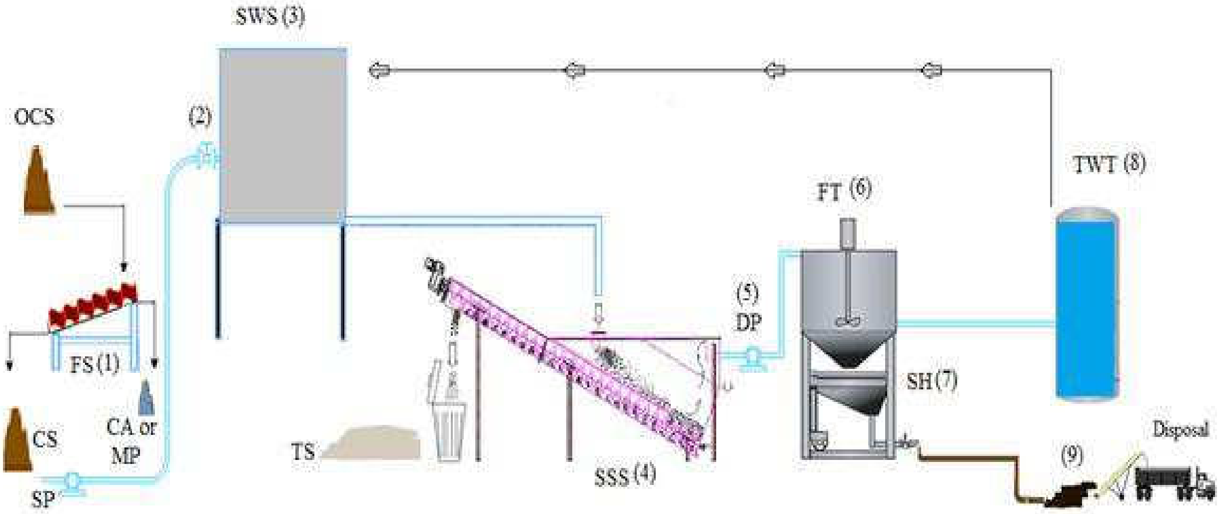

Fig. 1. Pilot plan for Soil remediation system.

3. RESULT

3.1 WASHING LOW CONTAMINATION

This study was focused on investigations of removed oil fromlow contamination sand. The washing procedure was repeated five timesa day to confirm the data obtained. As presented inTable (1), soil washing method showed that around 87 % of TPH was removed from the contaminated sand.

Tab. 1. Mean of TPH removal during the washing process. Note: The data are expressed as mean ± SD (n=5)

Sample ID	**TPH Before** (mg/kg dry weight)	**STD EV +/-**	**TPH After** (mg/kg dry weight)	**STD EV +/-**
1^{st} day	18,447	342	2157	156
2^{nd} day	22,050	322	2360	149
3^{rd} day	19,410	308	2010	135
4^{th} day	18,740	305	3180	140
5^{th} day	20,200	331	3647	197

This study demonstrated that the percentage reduction of TPHduring the pilot were non significantly different (A one-way $F (4, 20) = 76.1$, Post-hoc Scheffe tests, $p = > 0.05$). The results in this work, revealed that the washing system was effective in removing oil from contaminated soil and has potential capability in enhancing oil solubilisation.

3.2 WASHING MEDIUM CONTAMINATION

This study was conducted to determine the amount of TPH removed from medium contamination sand. The washing procedure was repeated five times a day. Moreover, Table (2) showed that around 90 % of TPH was removed from the contaminated sand.

Tab. 2. Mean of TPH removal during the washing process. Note: The data are expressed as mean ± SD (n=5)

Sample ID	**TPH Before** (mg/kg dry weight)	**STD EV +/-**	**TPH After** (mg/kg dry weight)	**STD EV +/-**
1^{st} day	44,456	396	4797	146
2^{nd} day	41,325	350	4937	84
3^{rd} day	46,244	384	4963	171
4^{th} day	46,870	335	4687	133
5^{th} day	42,800	369	4287	187

The provide a clear indication that the percentage reduction of TPH during the pilot were non significantly different (A one-way F (4, 20) = 63.6, Post-hoc Scheffe tests, p = > 0.05). This work indicates clearly that the greatest rate of oil removal from samples was achieved with higher oil contaminated sand.

3.3 WASHING HIGH CONTAMINATION

Soil washing was performed in an effort to determine the amount of TPH removed from medium contamination sand. Also, the washing procedure was repeated five times a day. Furthermore, Table (3) showed that about 90 % of TPH was removed from the contaminated sand. The provide a clear indication that the percentage reduction of TPH during the pilot were non significantly different (A one-way F (4, 20) = 24.1, Post-hoc Scheffe tests, p = > 0.05). As a result, the efficiency of the pilot was able to deal and reduce high concentration of TPH.

Tab. 3. Mean of TPH removal during the washing process. Note: The data are expressed as mean ± SD (n=5)

Sample ID	**TPH Before** (mg/kg dry weight)	**STD EV +/-**	**TPH After** (mg/kg dry weight)	**STD EV +/-**
1st day	65,830	377	5992	128
2nd day	61,220	332	6021	97
3rd day	64,322	314	6211	181
4th day	64,190	356	6821	143
5th day	63,366	373	6402	151

4. DISSCUSSION

This improvement can be associated with the increased length of time of the washing system. Therefore, the washing time was believed to correspond to the wetting of the soil with the water. Urum *et al.* (2004) reported that the wettability of contaminated soil and contact angle between the soil and oil increase with washing time. However,this project found that there was no-significant difference between medium contamination and high contamination (M = 226,450; SD = 8,856) (Post-hoc Scheffe tests, p = 0.777) after the washing process completed, see Figure 2.

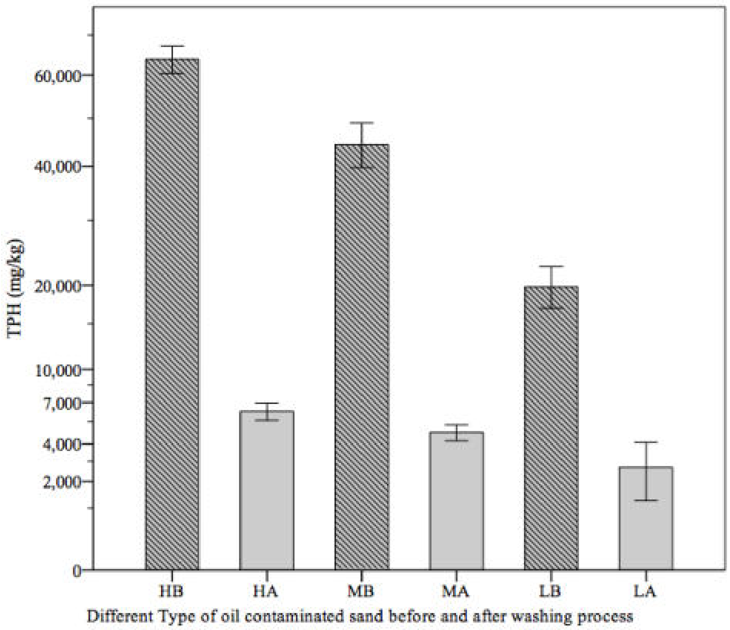

Fig. 2. Mean of TPH removal during the washing process. Note: (A) After; (B) Before; (H); High contamination; (M) Medium contamination, and (C) Low contamination. The data are expressed as mean ± SD (n=5).

The outcome of this study shown that the percentage of TPH removal was increased for low contamination sample, this slight removal of TPH could be attributed to the nature of weathered contaminated soil. This study was determined the amount of oil removed from 200 kg of Kuwait oil sand using the ratio of (mass: volume)

1:1.5. According to Chu and Chan (2003), soil washing was carried out to clean contaminated soil with hydrophobic organic compounds. They found that the soil washing was able to achieve an effective optimum washing condition using a soil to solution ratio of 1:6 (mass/ volume). However, this study shows that decreasing the soil/solution ratio to 1:1.5 (mass/ volume) enhanced the percentage of oil removal. Also, the volume of the wastewater produced after the washing processes complete was reduced to 50 %. These experiments indicate clearly that the greatest rate of oil removal from samples was achieved with a ratio of 1:1.5 (mass/volume).

5. CONCLUSION

The scenario in Kuwait is somehow exceptional as the contamination is primarily caused by crude oil, which has been weathered under open environment for 25 years. The exposure to the environment has caused most of the volatile substance within the crude oil to evaporate into the atmosphere with a heavy compounds left as residue. Due to the complex nature of contaminated soil and the undeniable fact that contaminations in different situation present of a "cocktail" of various types of pollutants, therefore, different types of remediation deals with different range of contaminates, limited success have been reported in remediation contaminated soil. Remediation of oil-contaminated soil in Kuwait were applied individually with different methods, with limited success with lengthy time process and high cost. This encourages the various investigators to carry out research to find new technique to reduce the concentrations of contaminates to satisfactory levels. This kind of work is vital for successfully meeting the remediation objective, with a system being chosen that offers cost effectiveness, feasibility and short time. This pilot is aimed to assess the efficiency of the new strategy for removing hydrocarbons from contaminated soil to acceptable level.

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REMOVING THE THREATS OF OBSOLETE PESTICIDES IN MOLDOVA

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KEYWORDS
Persistent Organic Pollutants (POPs), Obsolete Pesticides, Basel Convention, Moldova, Contaminated Sites, Safeguarding, Export, Disposal

ABSTRACT

Since 2011, DEKONTA has been responsible, in close cooperation with the POPs Centre of the Ministry of Environment of Moldova, to dispose approximately 752 tonnes of obsolete pesticides (and pesticides contaminated materials) from eight different warehouses in Moldova (Gradinita, Ciobalaccia, Clocusna, Pascani, Singerei, Oliscani, Pelivan and Paupati). The main goal of our projects has been to repack the waste into appropriate containers, clean-up the warehouses and to transport the contaminated waste for final disposal in incineration facilities in Europe.
In this paper, it will be presented the process of safeguarding illustrating the challenges encountered and lessons learned from the implemented projects in Moldova.

INTRODUCTION

For decades, pesticides have been used worldwide as a mean to increase agricultural output, fight pests and control tropical diseases. Now, obsolete, these chemicals are highly toxic, highly dangerous substances that pose a direct threat to human health. In Moldova, it is not uncommon for local residents to use the dismantled warehouses as building materials for their own sheds, houses and fences and even re-use obsolete pesticides for agriculture. It is clear that obsolete pesticides lying out in the open or in ruined stores can easily pollute the environment and are a risk to human health. For this reason, Moldovan authorities with the co-operation of international donors like FAO, NATO, the Czech Government and others, have implemented several projects with the aim to remove this threat from the environment.
Since 2011, DEKONTA has been co-operating with the Moldavian authorities and has removed 752 tonnes of obsolete pesticide waste from several pesticides storehouses in the country.

Tab. 1. Summary of DEKONTA's Projects in Moldova

Project	Date	Amount (t)	Summary
Remediation of environmental burdens caused by pesticides in Moldova - **Funded by Czech Development Agency**	09/2011 to 04/2013	202	Gradinita, Ciobalaccia and Clocusna storehouses Included capacity building Disposed in Germany
Remediation of environmental burdens caused by pesticides in Moldova II - **Funded by Czech Development Agency**	10/2013 to 06/2015	250	Singerei, Oniscani, Pelivan, Papauti storehouses Included capacity building Disposed in Germany
Safeguarding and Disposal of hazardous chemical waste in Moldova - **Funded by the Food and Agricultural Organization of the United Nations**	01/2015 to 09/2016	360,5	Pascani storehouse Project is running Included capacity building To be disposed in Poland

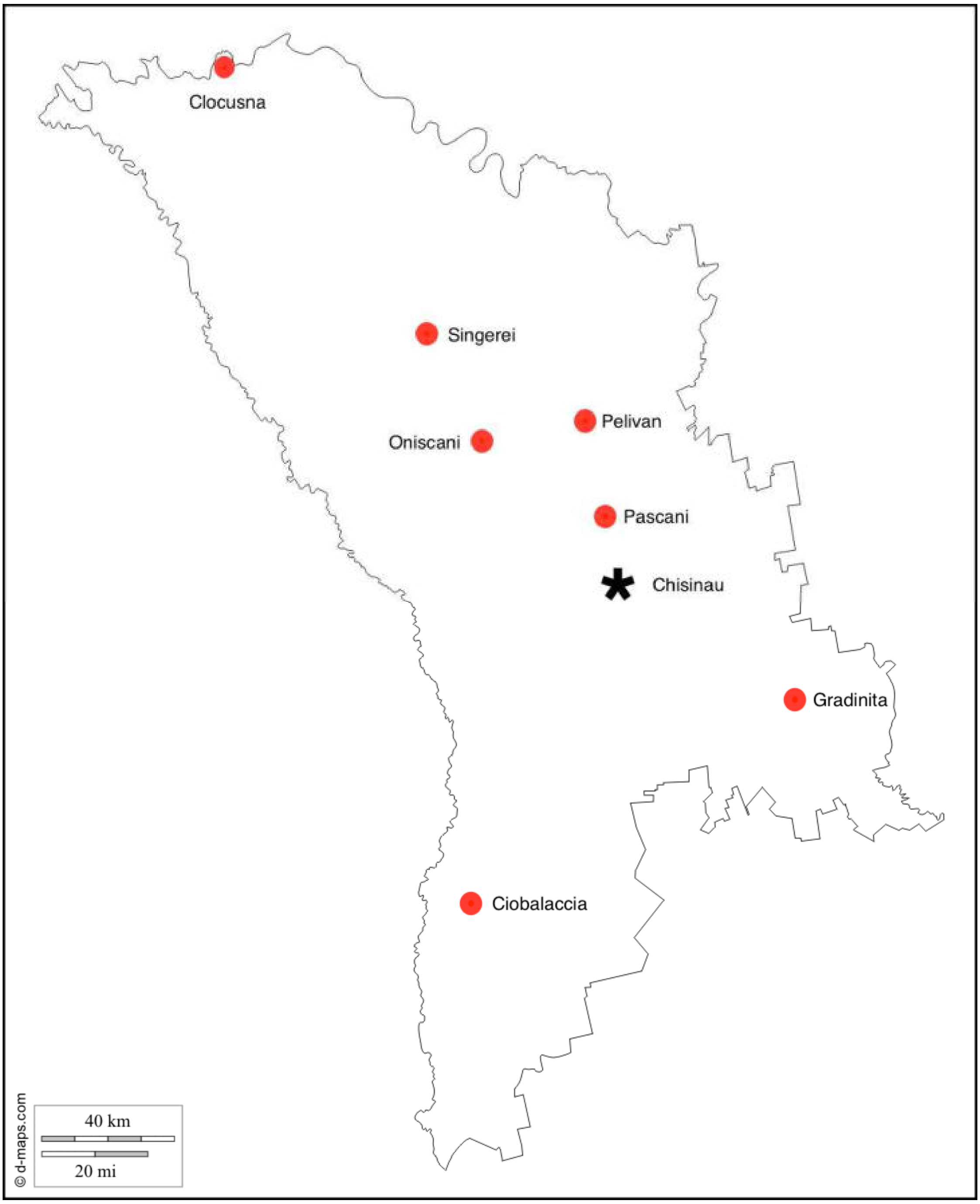

Fig. 1. Location of the Obsolete Pesticides Storehouses in Moldova.

DEKONTA’s approach for the implementation of the projects was divided in six main phases: health and safety plan elaboration, inventory, safeguarding, transportation, disposal and site hand-over.
A summarized description of the phases is illustrated in below:

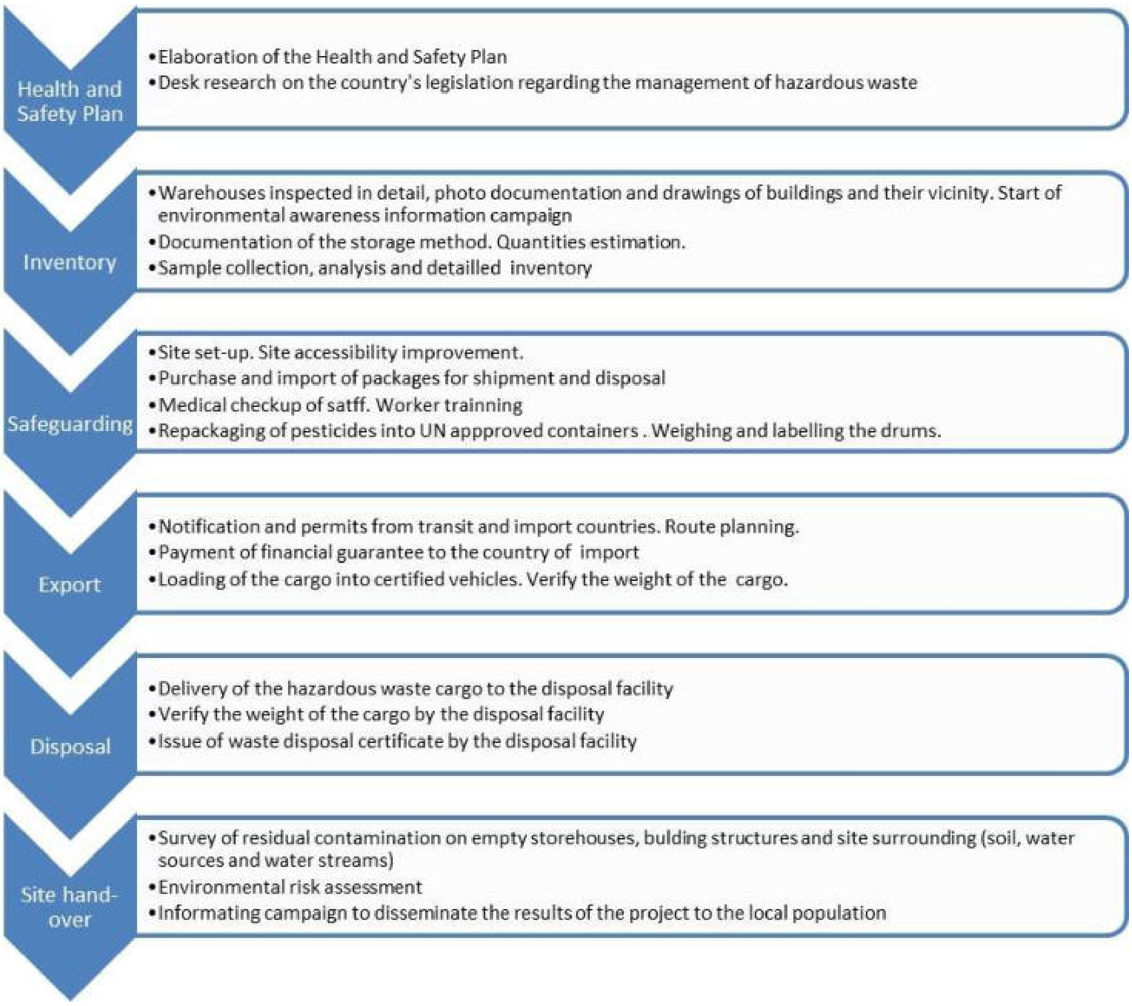

Fig. 2. Summary of the main phases of the project.

WASTE CHARACTERIZATION AND EXPORT

The results of qualitative analyses of pesticide samples and contaminated debris indicate presence of a wide spectrum of substances. The most represented pesticides in solid matrices include trifluralin, α, β, γ, δ – HCH, atrazine, carboxin, proparil (DCPA), diazinon, diphenamid, chlorobenzilat / chloropropylat / etoxinol, mefenoxam / metalaxyl, prometryn, propazine, simazine / triazine, sulfotep and triadimefon. Acetochlor, metochlor and atrazine, dimethachlor, propazine, simazine/triazine, terbuthylazine and 2,4,D were found in liquid matrices.
According to the analyses at the wastes were assigned codes according to the European catalogue of wastes (Decision of the Commission 2000/532/EC) and classes of hazardous character according to the European Agreement Concerning the International Carriage of Dangerous Goods by Road, the so-called ADR.
The export of the waste was done by road to the incinerators, the wastes were packed in plastic drums of various sizes for the solids pesticides, in jerrycans and plastic IBCs of various sizes for the liquid pesticides and in FIBCs (or Big Bags) for contaminated PPEs, soils and old containers.

CONCLUSION

The projects had very positive impact in the condition of the environment. The most benefitted group of these projects were the workers who move directly around the premises of pesticide warehouses, people who live in the surroundings of pesticide warehouses and the inhabitants of respective districts, who could be adversely affected by collected toxic substances, due to flue dust particles, improper handling, escape of liquids and etc.
As the direct benefits in the social sphere we can see the opportunity of an additional income of local inhabitants from auxiliary works associated with removal of wastes. These concerned miscellaneous small

repairs (of warehouses, tools and equipment, vehicles), transport of material, manual help when loading and unloading goods, guarding of buildings, forklift operation, etc.

The implementation of these projects proved to be challenging. The main challenges encountered were:

- ➢ Lack of information regarding the pesticides stored in the storehouses. Storehouses in very poor conditions.
- ➢ Presence of strong oxidizers in the storehouses. Permanent risk of fire.
- ➢ Routes for the transportation of the pesticides should be planned considering the countries of transit/import. Some authorities are quicker to approve the movement of the waste through/to their territory.
- ➢ Maritime transportation companies may refuse to transport the waste in their vessels.

The lessons learned from these projects were:

- ✓ Insisting on maximal safe conditions during the work. The presence of unknown substances and poses a constant threat for the safety of the workers.
- ✓ Strict usage of PPE and safety equipment at the site. Due to the uncertainties regarding the identities of the chemicals present at the site, DEKONTA´s approach is to be one step ahead and use more PPE than the minimum required.
- ✓ Detailed analysis in the field, cross analysis (Raman spectography and RTG) for the identification of unknown chemicals.
- ✓ Elemental analysis of every drum for presence of limiting elements regarding incineration limits.
- ✓ Close cooperation with analytical laboratory - identification of all chemicals including the metabolites of pesticides, specific pesticides that were tested in Moldova during the Soviet times

It is also necessary to mention that repackaging and disposal of the obsolete pesticides only removes the source of the contamination. It is common that residual contamination remains at the site (contaminated building structures, soil, water bodies and etc.) and it should also be addressed in future projects. As an example, soil samples (soil probes, surface soil) collected from the Oniscani site after the pesticides repackaging activities have been completed revealed concentrations above 50 mg/kg in soil, i.e. the level when materials are classified as hazardous waste according to the Moldavian regulations.

For this reasons, a comprehensive information campaign to raise awareness must be carried out until further projects addressing residual contamination are implemented. Situations were locals perceive the old storehouses, now empty of pesticides, as safe are not uncommon. In many cases building materials are at risk of being removed from the site and used as building material for houses or stables.

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SOME FEATURES OF SOIL CONTAMINATION BASED ON SOIL MONITORING SYSTEM IN SLOVAKIA

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KEYWORDS
Soil monitoring, soil contamination, contaminated sites, heavy metals

ABSTRACT

Risk elements distribution on agricultural soils in Slovakia is evaluated in this contribution. The measured results have been obtained on the basis of soil monitoring system in Slovakia which is consistently running since 1993 year. Risk elements have been analysed in extraction by aqua regia according to uniform analytical procedures in soil (Kobza et al. 2011). On the basis of the available results it may be said that the agricultural soils of Slovakia are not extensively contaminated except some contaminated sites which are mostly situated on the industrial areas (anthropogenic impact) as well as on the areas under geogenic influence. Their unfavourable state lasts often a long period and agricultural land use of those affected fields is not recommended.

In addition, it seems that the natural process of improvement of contaminated sites caused by human impact is very slow and on contaminated sites caused by geogenic influence is practically without significant change after 1990 year. It means the soils which were contaminated on the beginning of soil monitoring process, are contaminated also at present.

INTRODUCTION

Governmental soil policy of Slovakia declares that the soil is and will be the basics of environmental, ecological, economical and social potential of Slovakia and therefore it must be carefuly protected against damage. The new regulation concerning agricultural soils is the Act n. 220/2004 Z.z. on protection of agricultural soils and agricultural land use (MPSR, 2004) and Act n. 59 of Ministry of Agriculture and Rural Development of Slovakia from the 11.-th of March, 2013 (MPRV SR, 2013) in effort to increase quality and to integrate decision sphere concerning the protection of agricultural soils with the aim of their protection against degradation. For the better realisation of this regulation in the praxis, it will be necessary to know the actual state of soils and their development using the complexed soil monitoring system in Slovakia which has been running consistently since 1993 year.

Recently, environmental damages on the example of selected contaminated sites in Slovakia are described in this contribution.

MATERIAL AND METHODS

The obtained results are evaluated on the basis of soil monitoring system in Slovakia. Soil monitoring network in Slovakia is constructed on ecological principles and includes the research data of all main soil types and subtypes, soil substrates, climatic regions, emission regions, contaminated and non-contaminated regions as well as various land use. There are 318 monitoring sites on agricultural and alpine land in Slovakia. All soil monitoring sites are located in WGS 84 coordinates. The monitoring site represents the circular shape, with a radius of 10 m and an area of 314 m^2. The standard depths of 0–0.10 m, 0.20–0.30 m and 0.35–0.45 m on soils under grassland and 0–0.10 m and 0.35–0.45 m on arable land are sampled, but the depth is adjusted to characterize the main soil horizons. The soil monitoring in Slovakia is running in 5 years repetitions. The most important risk elements concerning soil contamination are included (Cd, Cr, Pb, Ni, Zn, Cu, Se, Co extracted with aqua regia) and Hg (total content). Methodical and analytical procedures were realized according to work (Kobza et al., 2011).

RESULTS AND DISCUSSION

The various impacts influencing on the evaluation of soil contamination could be described as follows:

- human influence (industry, agriculture, municipal waste materials, etc.);
- influence of geochemical anomalies;
- combined influence.

The human influence on contamination of soils in Slovakia (former Czechoslovakia) was the most significant after the Second World War and especially during the industrial period in the second half of the 20-th century.

The geochemical anomalies occur especially in volcanic and crystalline rocks, mainly in mountainous regions, this process is manifested in agricultural land with less intensity. The most extended areas of geochemical anomalies appear in Štiavnické vrchy, Low Tatras and Slovenské Rudohorie mountains. These regions are often characterized by high to very high concentrations of some risk elements, especially in all soil profile (Cd, Pb, Cu, Zn, As).

Tab. 1. Average content of risk elements (mg.kg^{-1}) extracted with aqua regia in arable layer (0 – 10 cm) of agricultural soils in Slovakia

Soils	As	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Se**	**Hg**
FM	10.8	0.7	8.8	39.1	34.0	37.0	54.3	122.8	-	0.2
ČA	10.0	0.4	7.8	42.9	22.7	29.6	21.1	75.6	0.2	0.06
ČM	10.0	0.4	7.8	42.9	22.7	29.6	21.1	75.6	0.3	0.1
HM	9.2	0.2	10.0	41.5	22.9	32.6	19.7	68.8	0.1	0.05
LM+PG	9.9	0.3	9.7	42.8	17.0	23.3	24.2	66.7	0.2	0.07
KM	14.8	0.3	12.6	52.2	28.9	29.2	27.0	93.5	-	-
RM	3.4	0.1	2.0	19.5	17.0	12.0	7.7	41.0	0.3	0.03
RA	13.1	0.5	11.8	55.2	30.6	42.0	36.3	103.1	-	0.13

Explanations: FM – Haplic Fluvisols, ČA – Mollic Fluvisols, ČM – Chernozems, HM – Cutanic Luvisols, LM+PG – Albeluvisols and Planosols, KM – Cambisols, RM – Regosols, RA – Rendzic Leptosols

Measured average values of risk elements are lower than valid hygienic limit for Slovakia (MP SR, 2004, MPRV SR 2013). These ones are running in the mean range of As: 3.4 – 14.8 mg.kg^{-1}, Cd: 0.1 – 0.7 mg.kg^{-1}, Co: 2.0 – 12.6 mg.kg^{-1}, Cr: 19.5 – 55.2 mg.kg^{-1}, Cu: 17.0 – 34.0 mg.kg^{-1}, Ni: 12.0 – 42 mg.kg^{-1}, Pb: 7.7 – 54.3 mg.kg^{-1}, Zn: 41.0 – 122.8 mg.kg^{-1}, Se: 0.1 – 0.3 mg.kg^{-1}, Hg: 0.03 – 0.2 mg.kg^{-1}. The distribution of risk elements depends on parent material, land use, soil type and potential source of elements origin (geogenic, anthropogenic, resp. mixed influence). Concerning the measured values of risk elements given in the Table 1 the slightly higher values of some elements (Cd, Cu, Ni, Pb, Zn, Hg) occur on the Fluvisols which could be transported from the catchments and accumulated on alluvial deposits.

Higher values of some elements are also characteristic for some Cambisols which are influenced by geochemical anomalies occurrence especially on crystalline rocks and volcanic deposits, as well. Therefore also mean values of some risk elements on Cambisols are also increased (As, Co, Cr, Cu, Zn).
On the contrary, the soils with low to very low content of humus and clay fraction (Regosols) are characteristic with the lowest content practically of all risk elements, what it was already mentioned in some previous works (Linkeš et al., 1997, Wilcke et al., 2005).

The significant change of risk elements was not observed during monitored period of last 20 years (Kobza, et al., 2014). It means that the soils which were contaminated at the beginning of soil monitoring process (1993 year), are still contaminated at present.

Soil contamination can create visible phenomenas (mostly in the surroundings of industrial areas) or non-visible effects (e.g. influence of geochemical anomalies). In the framework of the 1-st example the highest values of some risk elements are often measurable in the topsoil, but on the other hand in the areas of geogenic influence high to very high content of some risk elements occurs mostly in all soil profile, resp. their content can increase with depth of soil.

It may be said that antropogenically deposited heavy metals are less strongly bound in soils, because chemical equilibration of heavy metals in soils is a long-lasting process (Chlopecka et al., 1996, Wilcke and Kaupenjohann, 1997).

In addition, remarkable significance has also a „hidden“ soil contamination. It is soil contamination, where the contaminated soil-sedimentary material was covered by latest soil-sedimentary material during shorter or longer period and these areas are often intensively cultivated for agricultural production at present. This case can be presented on the following example in Horná Nitra region (Figs. 1and 2).

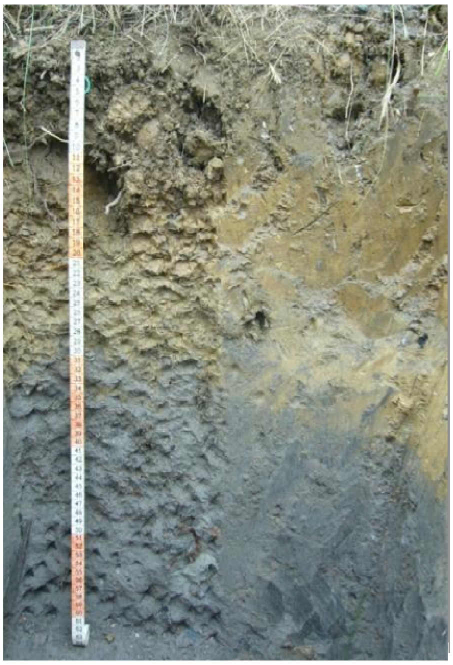

Fig. 1. Gray ash layer in soil profile of Fluvisol (Horná Nitra region).

Fig. 2. Contaminated site on agricultural land (Horná Nitra region).

This structure of soil profile is a result of strong storm in 1965 year, when the waste dam near Zemianske Kostolany was destroyed and gray ash very rich in arsenic was transported by rain water along the Nitra river. This gray ash layer is located in the depth of 40 – 45 cm (Fig. 1) with very high content of arsenic (near 900 $mg.kg^{-1}$) at present. Topsoil is agriculturally cultivated (Fig. 2) with also very high content of arsenic (near 200 $mg.kg^{-1}$) (Kobza et al. 2012).

In addition, the „hidden“ contamination often occurs in mining areas with its origin of the middle age, when by processing and cleaning mining ore the waste material with high content of risk elements has been distributed into the country. The result of these old human activities are contaminated sites situated also on agricultural land as well as in the settlements (in the middle age greenland) – on gardens and orchards, as well. Contaminated sites are also situated on the aluvial deposits of agricultural land along the rivers and brooks flowing from old mining areas. In the following table 2 the risk elements distribution is presented on Štiavnica stream.

Tab. 2. Risk elements distribution of contaminated site on aluvial deposits of Štiavnica stream (Dvorníky)

Soil depth	Risk elements in $mg.kg^{-1}$ (extracted in aqua regia)								
	Cd	Pb	Cu	Zn	As	Ni	Cr	Co	Hg[1]
0 – 10 cm	**9.94**	**1238.00**	**111.00**	**1191.00**	12.70	10.30	24.10	9.28	0.27
35 – 45 cm	**9.89**	**1941.00**	**137.00**	**1340.00**	14.30	5.35	15.30	14.00	0.10

1 – total content (TMA analysator)

Fig. 3. Fluvisol on Štiavnica stream (Dvorníky). **Fig. 4.** Contaminated site on agricultural land (Dvorníky).

Distribution of risk elements is a result of old mining activity in Banska Štiavnica region and their transport along the Štiavnica river into the agricultural land since the middle age period. Very high content of risk elements (Cd, Pb, Cu and Zn) was determined on monitoring contaminated sites on aluvial deposits of Štiavnica river (Fig. 3 and 4). These fields are not suitable for agricultural use (often in opposite reality), because the quality of agricultural crops could be affected.

CONCLUSIONS

In general, on the basis of the available results it may be said that the agricultural soils of Slovakia are not extensively contaminated except of some contaminated sites which are mostly situated in the industrial areas (anthropogenic impact) and under geogenic influence. Their unfavourable state lasts often a long period and agricultural land use of those affected fields is not recommended.

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NEW SYSTEM OF LIMIT VALUES FOR THE ASSESSMENT OF SOIL POLLUTION IN THE CZECH REPUBLIC

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KEYWORDS
Soil protection legislation, risk elements, risk substances, agricultural soil

ABSTRACT

New system of limit values was proposed as a Decree to the Agricultural soil protection Act amendment and it is valid since June 2016. The system consists of two levels of differentiated limit values: prevention and indication values. The prevention limit values are constructed statistically as the upper level of geochemical and anthropogenically diffused soil pollution and their main purpose is prevention of agricultural soils from further loading by potentially toxic substances. The indication limit values, on the other hand, are derived as worst case effect – based which means that the negative effects on human health or environment can appear in case of limit exceeding. Three different categories of indication limit values were specified according to exposition scenario: a) risk of food chain contamination; b) risk of phytotoxic effects; c) risk of direct effects on human health. Both prevention and indication limits are constructed for selected risk elements and persistent organic pollutants. System of soil sampling, analytical methods and measures in cases of limit exceeding are a part of the new legislation.

NEW SYSTEM OF SOIL LIMIT VALUES

The criteria for the assessment of soil pollution were adopted for the Czech legislation in 1994. In spite of the fact that they were just taken from different foreign legislative measures it was a good step forward at that time. However, after 22 years, they do not reflect present requirements of agricultural soil protection, as well as they are not consistent with European and world attitudes to prevent soil pollution.
The new system of limit values started to be constructed in 2002 already, based both on the previous works of national experts (Němeček et al. 1996; Podlešáková et al. 1996; Beneš 1993; Němeček et al. 2001; Podlešáková et al. 2001; Němeček et al. 2002; Podlešáková et al. 2002; Vácha et al. 2002) and contemporary international attitudes (EPA 2002; ISO 2005; LABO 1995). Construction of the new system followed two basic principles:

- to comprise scientific knowledge on the toxicity of elements and substances for humans and environment and their soil risk assessment,
- to be applicable in the legislation and state administration.

In order to interlink these principles the system of limit values was differentiated according to a) level of risk; b) exposition pathway; c) analytical method, reflecting the bioavailability of risk elements and d) soil properties.

Tab. 1. Scheme of the system of soil limit values

LEVEL OF RISK	EXPOSITION PATHWAY	ANALYTICAL METHOD	SOIL PROPERTIES
prevention	general prevention for humans and environment	aqua regia, total for Hg	two classes of soil texture for all elements
indication - risk elements	food chain contamination	aqua regia, total for Hg	two classes of soil texture for Cd
			three classes of pH for Cd and Ni
		1mol/L NH_4NO_3	two classes of soil texture for Cd
			two classes of pH for Cd
	plant growth inhibition	aqua regia, total for Hg	three classes of pH for Cu and two classes for Ni
		1mol/L NH_4NO_3	-
	human health protection	aqua regia, total for Hg	-
indication - persistent organic pollutants	human health protection	total content	-

PREVENTION LIMIT VALUES

The prevention limits were derived from background values of risk elements (RE) and persistent organic pollutants (POPs) in Czech agricultural soils analysed for RE individually for light texture soils and normal texture soils. The values for RE are not valid for specific geological substrates with their higher natural (geogenic) contents The purpose of prevention limits is to protect soil from increasing of RE and POPs contents coming from both intentional and unintentional application of substances on agricultural soils. The prevention limits have already been applied in legislation in cases of sewage sludge and sediments utilization: it is not allowed to apply them on soils where prevention limits were exceeded.
Tables 2-3 shows preventive limit values as adopted for legislation.

Tab. 2. Proposed RE prevention limits in agricultural soils

	Prevention value (mg/kg of d.m.)										
Soil Category	As	Be	Cd	Co	Cr	Cu	Hg	Ni	Pb	V	Zn
Standard texture soils[1)]	20	2,0	0,5	30	90	60	0,3	50	60	130	120
Light texture soils [2)]	15	1,5	0,4	20	55	45	0,3	45	55	120	105

[1)]Soils except light texture soils
[2)]Sandy soils, loamy-sandy soils, gravel-sandy soils

Tab. 3. Proposed POPs prevention limits in agricultural soils

POPs	Prevention value (mg/kg of d.m.)
Polycyclic aromatic hydrocarbons	
Σ PAHs[1)]	1.0
Chlorinated hydrocarbons	
Σ PCB [2)]	0,02
Σ DDT [3)]	0,075
HCB[4)]	0,02
HCH[4)] (Σ α+β+γ)	0,01
PCDDs/Fs[5)]	5,0
Petroleum hydrocarbons	
Hydrocarbons C10 – C40	100

[1)]Σ PAHS – polycyclic aromatic hydrocarbons (anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, phenanthrene, fluoranthene, chrysene, indeno(1,2,3-cd)pyrene, naphthalene, pyrene)
[2)]Σ PCB congeners – 28+52+101+118+138+153+180
[3)]Σ DDT, DDE, DDD
[4)]HCB and HCH (Σ α+β+γ) – analysed only by suspicion of their contents in soil
[5)]International toxic equivalent value (I-TEQ PCCDs/Fs) (ng/kg of d.m.) – analysed only by suspicion of increased PCDDs/Fs contents in soil

INDICATION LIMIT VALUES

The indication limits are constructed as effect based, i.e. some adverse effects can be observed when the contents of substances in soil are higher than the limit value, considering the safety factor and worst case scenario. According to the legislation, some measure must be done in case of indication limit exceedance, including site specific risk assessment procedure. The specific category of the limits must be used, according to the given land use and exposition scenario. Where the limits are set for aqua regia and NH_4NO_3, the limit is considered as exceeded if both extracts are exceeded.
Tables 4-7 shows indication limit values as adopted for legislation.

Tab. 4. Indication limits of food chain contamination

Element	Soil texture	pH/$CaCl_2$	Indication value (mg/kg of d.m.)	
			Aqua regia	1mol/L NH_4NO_3
As	-	-	40,0	1.0
Cd	-	≤ 6.5	1.5	-
	standard texture	> 6,5	2.0	0.1
	light texture	> 6,5	2.0	0.04
Ni		≤ 6.5	150	-
		> 6,5	200	-
		-	-	1.0
Pb		-	300	1.5
Hg*		-	1.5	-

*Total content by AMA method

The exceeding of limit value is valid in the case of any exceeding, a) Aqua regia extraction, b) 1mol/L NH_4NO_3 extraction when both analyses must be done if the limit values are available

Tab. 5. Indication limits of plant growth inhibition

Element	pH/$CaCl_2$	Indication value (mg/kg of d.m.)	
		Aqua regia	1mol/L NH_4NO_3
Cu	<5	150	-
	5 – 6.5	200	-
	> 6,5	300	-
	-	-	1.0
Ni	≤ 6.5	150	-
	> 6,5	200	-
	-	-	1.0
Zn		400	-
		-	20

The exceeding of limit value is valid in the case of any exceeding, a) Aqua regia extraction,
b) 1mol/L NH_4NO_3 extraction when both analyses must be done if the limit values are available

Tab. 6. RE indication limits of human health protection

Element	Indication value (mg/kg of d.m.)
As$^{1)}$	40
Cd$^{1)}$	20
Hg$^{2)}$	20
Pb$^{1)}$	400

$^{1)}$Aqua regia extract – valid for all soil texture categories
$^{2)}$Total content by AMA method

Tab. 7. POPs indication limits of human health protection

Substance	Indication value (mg/kg of d.m.)
Σ PAHs$^{1)}$	30
Benzo(a)pyrene	0,5
Σ PCB$^{2)}$	1,5
Σ DDT$^{3)}$	8,0
HCB$^{4)}$	1
HCH$^{4)}$ (Σ α+β+γ)	1
PCDDs/Fs$^{5)}$	100

$^{1)}$Σ PAHS – polycyclic aromatic hydrocarbons (anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, phenanthrene, fluoranthene, chrysene, indeno(1,2,3-cd)pyrene, naphthalene, pyrene)
$^{2)}$Σ PCB congeners – 28+52+101+118+138+153+180
$^{3)}$Σ DDT, DDE, DDD
$^{4)}$HCB and HCH (Σ α+β+γ) – analysed only by suspicion of their contents in soil
$^{5)}$International toxic equivalent value (I-TEQ PCCDs/Fs) (ng/kg d.m.) – analysed only by suspicion of increased PCDDs/Fs contents in soil

VALIDITY

The system of limit values has already been issued in Collection of Laws and is valid since the 1st June 2016 as Decree No. 153/2016 SB. System of soil sampling, analytical methods and measures in cases of limit exceeding are part of the legislation.

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CONTAMINATED LAND AND AGRICULTURE IN ENGLAND: AN OVERVIEW

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KEYWORDS
Agriculture, contaminated land, risk assessment, rural development

ABSTRACT

During the past 60 years the British agricultural industry has been undergoing significant economic and technological changes resulting in many small to medium sized undertakings ceasing to exist thereby providing a potentially extensive greenfield/brownfield land bank for rural re-development. This paper initially explains the UK Government's Part 2A contaminated land regime, (enacted 2000) examining its relevance to and impact upon agricultural land. Consideration is given to both active farmsteads within the Part 2A context and also contaminated land issues affecting post site closure re-development. The pre and post year 2000 situation is discussed focussing on the principle identified causes of contamination, i.e. fuel storage, fertiliser/agrochemical use and particularly waste disposal (farmyard, sewage and municipal). Undertaking contaminated land management and risk assessment in accordance with the published "Model Procedures" (2004) is discussed, commensurate with “normal” contaminated sites associated with past industrial activity. But whilst crops and livestock feature as Part 2A receptors risk assessment remains an un-exact science and there are no known cases of actual impact. With regard to redevelopment, risk perceptions can differ amongst regulators. Natural background “contamination” in agricultural soils is also an issue to consider. Case studies are presented.

INTRODUCTION

Prior to the 1970s in the UK, polluted land had neither been a governmental issue nor one of concern to the general public. With the expansion and intensity of the industrial revolution from the 1800s onwards, air and water pollution and impacts on the quality of life quickly grew to become major technical and legislative issues as evidenced for example by the first Alkai Act (1863), the Clean Air Act (1968, industrial chimneys) and controlling discharge of ammoniacal liquor from coal gas works into surface water courses. However, despoiled and derelict industrial land and whatever harboured within was not considered a problem, areas readily accepted as a necessary evil and agricultural land was clean, green and pleasant. Prior to 1959 no grants or funding was available to reclaim such land and serious dangers lurked as evidenced by the Aberfan disaster (1966) when a coal spoil heap engulfed a school with major loss of life.

Land was continually mistreated; wastes of whatever hazardous nature and toxicity could be deposited in any hole in the ground. However, the Part 1 of the Control of Pollution Act 1974 (England and Wales) first invoked waste control further strengthened over the decades in compliance with EU Directives. The Act also invoked legislative controls for both water and atmospheric pollution together with noise nuisance. In consequence of an explosion at a residential property in Derbyshire (England) in 1986 potential risks from landfill gas became a matter for risk assessment and control through Waste Management Paper 27 (WMP27) published in 1991 and The 1995 General Development Order. Heavy metals in residential garden soils became an issue in the late 1970s when high concentrations where discovered in Shipam Village where new housing had been built in the 1960s on former metalliferous mining land. In September 1981 the New Scientist published an article reporting that government scientists were warning of hundreds of lives at risk through building housing of former gas works sites.

With growing concern over contaminated land, the (former) Department of the Environment (DoE) established the Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL) to offer advice to Local Authorities (LAs) publishing a series of eight guidance documents from 1983 to 1990. In 1995 the DoE also published a series of 47 documents, the Industrial Profiles, each describing the particular nature of a specified industry and the types of contaminants likely to BE associated with the processes. The Agricultural Industry was not included. To aid risk assessment in developing sites with regard to human health one ICRCL document introduced the Trigger Concentration concept, a series of Threshold and Action values and for a range of inorganic and organic elements and substances. In simple terms, a soil with concentrations below a particular Threshold would be considered safe and if above an Action, remediation measures required. These were withdrawn in 2004 and subsequently replaced by different sets of soil risk assessment criteria for human health including the Soil Guideline Values (SGVs) and others.

THE PART 2A REGIME

There has been no real definite figure as to the number, type and location of contaminated sites throughout the UK. Data issued in 2005 estimated 325,000 sites covering 300, 000 hectares. Compiling registers of potentially contaminated sites in England and Wales had begun to be considered once the potential risks began to come to light. In 1987 the Welsh Office made available to both LAs and developers an on-line database of possible risk sites greater than 0.5hectares in area. In 1990 The House of Commons issued the First Report on contaminated land urging that registers should be complied without further delay. However it would be some time before action was taken primarily due to concerns over housing blight.

Finally, in April 2000 the Environmental Protection Act 1990 (EPA 90) was enacted through Part 2A of the Environmental Act 1995 and commonly referred to as the Part 2A (contaminated land) regime. This primary legislation was supported by the Contaminated Land Regulations (2000) and both statutory and non-statutory guidance. The legislation provided a statutory legal definition in that contaminated land is any land which is in such a condition, by reason of substances in, on or under the land that – (a) significant harm is being caused or there is a significant possibility of such harm being caused or (b) significant pollution of controlled waters is being caused, or there is a significant possibility of such pollution being caused. Part 2A solely addresses historically contaminated land and the current use. It concerns what might have passed into ground/soil strata or water bodies from past activities and possible negative impacts, primarily upon human health albeit from chronic exposure but also harm to ecological systems and man's property. The regime is designed to ensure clean up of sites which present serious risks and which would or could not be dealt with either through the planning and re-development process or voluntary action. The regime excludes what is termed "normal contamination" and which encompasses natural background levels, diffuse pollution and contamination caused other by industrial activity.

Given the emphasis on human health the responsibility for administering the regime was adopted by each and every Local Authority Environmental Health Department (EHD) in England (326) and Wales (22). Each EHD formulated a Contaminated Land Inspection Strategy from which a database of low-medium and high-risk sites was established. Not surprisingly, database numbers differ as to whether or not an EHD's area is predominantly rural or urban/industrial and opinions have also differed as to what type of site should be included most notably with potentially low risk sites. Databases were principally created through consulting historical maps and plans. The next step was to undertake detailed inspections of high-risk sites and establish whether or not the land might meet the statutory definition, a process referred to as Determination and, if so, thereby warrant immediate remediation. Whole databases have not been placed in the public domain though enquiries can be submitted for individual sites.

From 2000 onwards, Part 2A gathered pace albeit within the normal constraints of money, time and manpower. Most every EHD established a dedicated post, the Contaminated Land Officer (CLO). Funding was made available from central government to undertake detailed inspections, risk assessments and remediation. Revised statutory guidance was issued in 2012 and which introduced the concept of four contaminated land categories: CL1 embodying land likely to be determined, CL4 definitely uncontaminated and with CL2 and CL3 as intermediaries. To assist with CL4 categorisation, screening values have been developed for arsenic, benzene, benzo-a-pyrene, cadmium, chromium VI and lead relative to six land use scenarios.

In 2016 the Environment Agency (EA) issued its third report on the state of contaminated land in England. This presents the results of a 2014 survey and charting Part2A progress achieved from 2000 to 2013. Millions of pounds have been spent with 511 sites determined and most now remediated, though before the CL4 concept was introduced. Not surprisingly, human health risk has been the main driver with arsenic, lead and benzo-a-pyrene (BaP) being principle contaminants of concern. The data should also be treated with some caution as not perhaps presenting such a comfortable scenario. Only 60% of LAs responded with some not answering all questions. Further still, many sites constitute individual residential properties within a single defined area, each property having been determined on an individual basis. In some cases, determination leading to clean up has been invoked to err on the side of caution and not necessarily robust scientific evidence, the classic case being with BaP. Without doubt, progress has been made and some seriously high-risk sites identified and appropriately remediated. However all LAs are now facing severe financial cutbacks in all services including environmental health Central government funding to assist LAs undertake inspections and remediation has not only been drastically reduced but is to be completely withdrawn in April 2017, an action severely criticised in a House of Commons' report on Soil Health (May 2016). There is now grave concern as to how a LA might be able to meet its ongoing and future statutory responsibility to administer the Part 2A regime. The complacency appears to be that the development process might come to the rescue

RISK ASSESSMENT

Compared to the days of the few ICRCL documents and limited landfill gas guidance, there is now a plethora of technical and non- technical information to aid and abet the legislators, consultants, developers and other interested parties. The key document however is that published in September 2004 as Contaminated Land Report 11 and entitled Model Procedures for the Management of Land Contamination, commonly just referred to as the model procedures. It sets out the principles common to either identifying and remediating possible Part 2A sites or redeveloping land as might be affected by contamination.

Contaminated land risk assessment is fundamentally based on the source – pathway – receptor concept. All three components must exist to constitute a contaminant linkage and in the case of a Part 2A site, that linkage must be significant for land to be legally determined. At its basic, there must be a single contaminant present in the upper 1.0m soil strata as could impact upon a receptor through a viable pathway. In the case of human health, exposure to contaminated soil encompasses direct and indirect routes through inhalation, ingestion including edible produce and skin contact. A linkage will not exist if one or more component is absent and conversely, remediation seeks either remove or reduce the intensity of a source, break a pathway or, if practicable, remove a receptor or substitute for a less sensitive end use. Contaminant linkages are built into a Conceptual Site Model (CSM) and which represents the possible risk(s) within a site and who or what is at risk.

When nothing is known about a site as if often the case the very first step is to undertake a detailed Phase 1 risk assessment or a desk study as commonly referred to. It is a qualitative assessment only, not involving soil sampling and chemical analysis. The exercise seeks to acquire information on sources, receptors and pathways through combining data collection pertaining to historical/current land use with a detailed site reconnaissance (walk over survey). The latter is important to record overall site characteristics and any particular abiotic and biotic features as might be indicative of possible contamination, especially small features (e.g. tanks) and land surfaces (e.g. hydrocarbon staining) which cannot be shown on historic maps and plans. Plausible contaminant linkages as might exist are thus identified and a Preliminary CSM formulated on which further actions are based embodying Phase 2 intrusive surveys incorporating generic and detailed quantitative assessment perhaps then leading to remediation. The CSM must consider all possible sources and receptors both within the subject site and adjoining/nearby land.

CONTAMINATED LAND AND AGRICULTURE

From the 1950s onwards British Farming practices began to dramatically change as governments encouraged home produced food self-sufficiency. In some ways, this mimicked the Industrial Revolution with technological advances in mechanization, use of agrochemicals and, in recent times, farm size. As with that revolution there began to grow environmental concerns. In 1971a Royal Commission issued its First Report addressing overall air, land and water pollution within the UK discussing the various sources and potential impacts of concern. With regard to agriculture, three common types of agricultural wastes were identified as presenting potential problems namely pesticide/herbicide residues in soils and edible crops, surplus fertiliser leaching into rivers and lakes and excreta from intensive animal production. In the subsequent years statutory and non- statutory controls have been introduced to reduce/prevent pollution through the mismanagement of substances and deleterious impacts on soil and water systems from wastes and agrochemicals. Since 1989 sewage disposal to agriculture land has been regulated to ensure heavy metal concentrations are not exceeded in soils; nitrate vulnerable zones have been established, Codes of Good Agricultural Practice for air, land and water published and environmental permitting for intensive pig and poultry units are now a requirement.

With regard to agricultural land, the overriding general theoretical contaminant linkages within the Part 2A regime is that natural soils may have become contaminated by inorganic or organic substances to a high degree such that there could be risks of phytotoxicity to commercial crops grown for both human and animal feeding stuffs, health to grazing livestock and ultimately, risks to human health within the food chain. This was the subject of an information note the (former) Ministry of Agriculture Fisheries and Food (MAFF) forwarded to all LAs in 2000 with the intention of providing advice to assist with formulating Inspection Strategies, identifying where contamination of agricultural land might exist and how it might be dealt with over and above other controls already in place. MAFF considered that in the main, any significant contamination as might be identified would be a result of natural background levels or wastes from historic metalliferous mining but, whatever nature of any contamination as might be detected in land as a Part 2A assessment, simple management practices would be the key to mitigating risks. Before Part 2A, ICRCL 70/90 had been published (1990) specifically addressing risks from mine spoil impacted soils. It presented Threshold and Action Trigger concentrations for arsenic, cadmium, copper, fluoride, lead and zinc with respect to both phytotoxocity and risks to grazing livestock.

The Statutory Guidance includes crops and livestock as Property Systems Effects. Significant harm would represent a substantial diminution in yield or loss in value resulting from death, disease or other physical damage. If either is caused by a contaminant linkage, a 20% reduction would be adopted as a benchmark to determine land as Part 2A. The complexities of soil-plant interactions and environmental factors clearly indicate such an exercise would be extremely difficult and deeply fraught with practical and scientific issues. Evidence to date for the UK indicates that metal concentrations in food and feed for a range of heavy metals have not exceeded maximum concentration values (McGrath 2015).

The MAFF document inferred it unlikely that agricultural land could constitute Part 2A land and as far as it is aware, no one site in England has been determined due to significant risks associated with crops and livestock from contaminants in natural soils or any likely to be in the future, particularly given the downturn in LA activity. The scientific parameters are complex, food safety is monitored under different legislation and risk assessment costs would be high since only Phase 2 assessments would provide the finite answers and then involving a multi-disciplinary technical team.

CONTAMINATED LAND AND RURAL DEVELOPMENT CONTROL

The UK coal gas industry was nationalised in 1947. During subsequent years a myriad of small to medium holdings were closed right up to the final demise of the industry in the 1970s. Hundreds were located in rural areas. Many, many sites have been redeveloped, some long before contamination was considered an issue until later years. ICRCL publication 18/79 provided information for the redevelopment of gasworks sites. The English agricultural industry has also undergone similar changes with the number of holdings decreasing by 45% over a 42 year period particularly smaller sites with a 50% reduction of those less than 50 hectares. As production ceased land became available for redevelopment.

Tab. 1. Agricultural Holdings in England (x1000)

Year	Total	<50 Ha
1972	186.2	139.8
1988	156.6	103.7
2005	132.4	84.2
2014	102.9	57.3

Within an LA the planning department will consult the EHD on contaminated land matters and planning applications. If there is any suspicion that an area of land might be contaminated and present risks to the future intended use, especially if a site is included on the Part 2A database, the EHD will advise that conditions are imposed to ensure a phased risk assessment is undertaken. This approach reflects the National Planning Policy Framework (NPPF) guidance (2012) invoking responsibility on a developer to ensure a site is fit for purpose with no unacceptable risks from contamination. There is usually no doubt about brownfield sites with former industrial use but opinions differ as to agricultural land and establishments both with developers and planning legislators. A developer does have the opportunity to submit information with an application, notably a Phase 1 report which, if approved could offset conditions being attached, but more often than not this does not occur, especially for a site where contamination issues might appear to be irrelevant.

A redundant agricultural enterprise will typically comprise a nucleus of buildings within a set curtilage and outlying fields, the latter which might be retained as arable or pasture land. Redevelopment will therefore often encompass the buildings, either as conversions or demolition and new build, more often to residential end use with private garden areas. An EHD would consider this as a highly sensitive end use from the human health risk perspective. However there would appear to be inconsistency as to what extent of risk assessment should be undertaken. By example, one South Cumbrian planning authority does not stipulate risk assessment for barn conversions whilst one in mid Lancashire always requires full detailed Phase 1 reports, incurring greater expense as might otherwise be justified. This reflects the different perceptions towards contaminated land held by different EHD officers. Other councils however have adopted a compromise whereby a developer has the opportunity to submit information by way of a simple questionnaire. This aims to ascertain the possibility of contamination being present from the use of buildings and land where substances could have entered ground strata. Table 2 presents typical questions.

A questionnaire in itself represents a very basic desk study but without the companion walk over survey. If all answers are negative then it would be perceived no contamination issues prevail and therefore no requirement for further action. This approach does however rely on the integrity of the persons completing the document. It would seem logical to retain the documentary approach but also incorporate a site reconnaissance report to present further evidence ideally by way of a photographic record.

Fig. 1. Redundant farm buildings scheduled for residential redevelopment.

Tab. 2. Issues relating to contamination in agricultural land

Any fuel storage, both above and below ground?
Any filled pits, farm tip or bonfires?
Any chemical storage such as fertilisers, pesticides, herbicides?
Any foot and mouth burial sites?
Any asbestos materials e.g. roof sheeting?
Any utility services?
Any cesspits, oil interceptors or electric sub stations?

Potential impact on any new development scheme from hazardous ground gases should also be considered including naturally occurring radon if the site is located within a radon affected area. WMP27 introduced the concept that any proposed development located within a 250m radius of a former or active waste disposal site might be at risk from landfill gas migration and which is still the adopted norm. In decades past hundreds of former marl pits and ponds were created in agricultural land and which were filled in over the years. Although these inevitably constitute very low risk potential gas sources due to their small size, the volume and type of waste deposited and age such features should nevertheless be considered and appropriate risk assessment undertaken.

In consequence of NPPF and government policy to build new homes throughout the country, development schemes are now underway on many green field sites, former agricultural land. Be it for on-site reuse or offsite disposal as surplus to requirements the quality of both topsoil and sub soil can only be determined via sampling and testing and unless there is documentary evidence counteracting suspicion, analytical suites should include pesticide and herbicide parameters. Whilst not a Part 2A issue natural contamination should ideally be considered and possible risks from elevated background concentrations if only to discount the matter as irrelevant. At present there is no standard practice or guidance regarding residential redevelopment on former agricultural land.

In conclusion, be it pollution impact on the environment or contaminated land issues and redevelopment, the risks from agricultural land are reasonably well understood and addressed on an ongoing basis. Under the Part 2A regime no site has been determined due to substances within indigenous ground strata. Past farm sites are not likely to constitute serious unacceptable risks to redevelopment on former agricultural land providing that a practical and pragmatic approach is taken both by legislators and developers working in conjunction. Non pollution issues of greater importance affect soils not least of all wind and water erosion.

Fig. 2. Former barn conversion to residential use.

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THE STUDY OF POPS CONTAMINATED SITES IN DANUBE RIVER BASIN OF REPUBLIC MOLDOVA FOR RISK ASSESSMENT AND REMEDIATION ACTIONS

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KEYWORDS
POPs contaminated sites, risk assessment, remediation of polluted soil.

ABSTRACT

The inventory of POPs polluted sites was made in Republic of Moldova in 2009 – 2010 years for the determination of needed management and remediation actions. The methodology of environmental risk assessment (ranking system) on regional level and local level (conceptual model) for individual sites is discussed. The case studies for Danube River basin were demonstrated used methodology.

INTRODUCTION

The inventory of old pesticide storages in Republic of Moldova, executed by Ministry of Environment and World Bank in 2009 – 2010 years, showed a large quantity of polluted sites (near 1500) remains after the repacking and evacuation project. More that 15 % sites were determined as extra high polluted territory with the POPs concentration in soil exceeding 50,0 mg/kg. They include some of the world's most harmful chemicals including highly toxic pesticides such as HCH, DDT; industrial chemicals such as PCBs, other toxic substances like PAHs, trifluralin, triazines, etc.

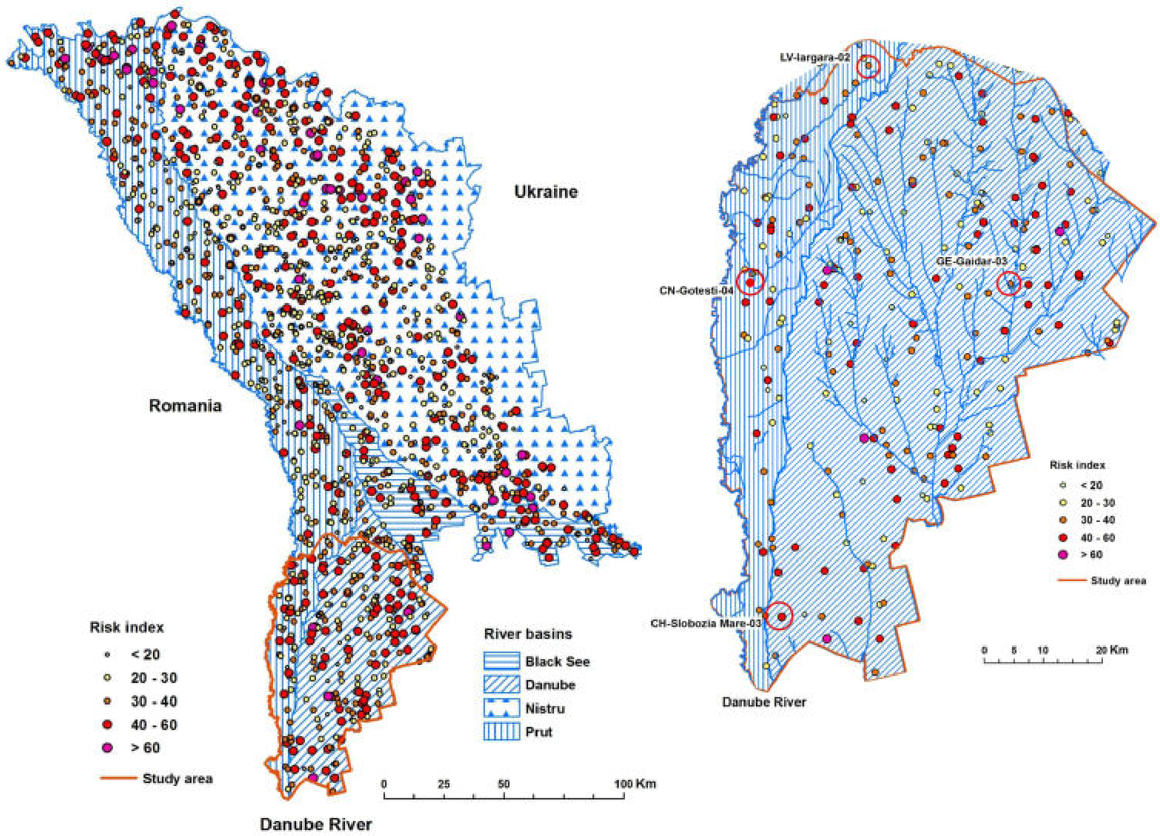

Fig. 1. POPs contaminated sites in Republic of Moldova a) area of the case studies b) Methodology of risk assessment on regional and local levels.

The rapid environmental risk assessment procedure was elaborated for the ranking of all polluted sites by the potential danjerous for the environment on regional level. This method is an approach for rapid classification of large number of polluted sites. Three principal factors of risk assessment were taken into account: first – level and pollution spectrum; second – risk receptors; third – distribution potential. First factor includes a concentration of toxic substances and pollution spectrum. Risk indexes for these factors are presendet in table 1. The final value of pollition risk coefficient was calculated after the determination of number of toxic substances. This coefficient depends of number of toxic substances (table 2).

Tab. 1. Value of risk indexes for pollution level

Category	Concentration / MAL*	Grade
Not polluted	below of detection limit	0
Admissible pollution	detection limit $\leq C \leq 1$ MAL	2
Small pollution	1 MAL < C < 10 MAL	4
Moderate pollution	10 MAL $\leq$ C < 100 MAL	6
High pollution	100 MAL $\leq$ C < 500 MAL	8
Very high pollution	500 MAL $\leq$ C < 5000 MAL	10
Extreme pollution	C $\geq$ 5000 MAL	14

* MAL for soil 0,1 mg/kg

Tab. 2. Value of risk coefficient for number of toxic substances

No. of substances	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Risk coefficient k	1,0	1,1	1,2	1,3	1,4	1,5	1,6	1,7	1,8	1,9	2,0	2,1	2,2	2,3

The formula of risk coefficient calculation for the level of pollution is:

$$Ip = (\Sigma\ Ip_1 + \ldots + Ip_i) * k \qquad (1);$$

where Ip_i - grade of risk for individual toxic substances; k – coefficient for number of toxic substances.

Risk receptors include two factors: distance of risk receptors to polluted site; importance and vulnerability to every receptors. The distance classification is presented in table 3. The every receptors is classificated in table 4.

Tab. 3. The value of risk indexes for distance to risk receptors.

Zone name	Distance from receptors to polluted site	Grade
Direct contact	0 m – 25 m	14
Guarantee contact	26 m – 50 m	10
Probable contact	51 m – 100 m	8
Low contact	101 m – 200 m	4
Insignificant contact	201 m – 300 m	2

Tab. 4. Risk indexes for different risk receptors.

Risk receptors	Grade
Forests, forest plantations, forest belts	1,2
Wetlands and flood zones	1,1
Rivers and springs	1,2
Lakes	1,2
Unused lands	1,1
Agriculture lands	1,2
Multiannual plantations (gardens, vineyards)	1,2
Localities	1,5
Job places	1,4
Water sources: wells, boreholes, springs	1,4
pastures	1,3

Value of risk receptor indexes is calculated by formula:

$$Ir = Ir_1 * w_1 + \ldots + Ir_i * w_i \qquad (2);$$

Where: Ir_i – risk index for distance to receptors; w_i – risk index for type of receptors.

Risk index for distribution potential includes particularities of site for the distribution of toxic substances to the environment. There are several ways of dispersing pollution in the environment: wind dispersion; infiltration to groundwaters; surface runoff; dispersion by animals and atropologic factors. The calculation of risk value is considered balance between factors to increase or decrease of pollition potential. Value of risk indexes for distribution potential is presented in table 5 and calculated by the formula:

$$Id = Id_1 * m_1 + \dots + Id_i * m_i \qquad (3);$$

where: Id_i – risk index for contributing and complicating factors of pollution dispersion; m_i – magnitude of distribution potential (table 5).

Tab. 5. Value of risk indexes for distribution potential (magnitude m).

Way of pollutant migration	**Grade**
Wind	8
Infiltration to ground water	3
surface runoff	6
dispersion by animals and atropologic factors	2

The total risk value is calculated by the formula which includes all three factors:

$$It = (Ip/100)*a + (Ir/100)*b\ (Id/100)*c \qquad (4);$$

where Ip – Pollution index; Ir – Risk receptors index; Id – Distribution potential indexes. Coefficients a, b, c are empirical coefficient. In our case a = 50, b = 30, c = 20.

The site ranking procedure in our study is not the same as risk assessment procedure. The examples of ranking systems are presented in EU, USA and Canada [1, 4, 5, 6]. The result of this ranking system is presented at site of Ministry of Environment http://pops.mediu.gov.md/ (fig. 1 a).

The environmental risk assessment on local level for every contaminated site should to formulate "conceptual model" of the pollution fate to risk receptors. This procedure has following key steps: 1 – hazard identification; 2 – consequences identification in the case when the hazard occurred; 3 - estimating the magnitude of the consequences (spatial and temporary); 4 - estimation of the consequence probability or the exposure assessment; 5 – the evaluation of risk importance (risk characteristic or assessment. The fate study of pollutants from source to risk receptors is a principal task of this model. In the case where is not a way of toxic substance migration to risk receptors there are no any risks. The risk management can be realized by several modes: the reduction or modification of pollution sources; managing or elimination of migration pathways; receptor modification.

Four sites were studied for the local risk assessment (figure 1 b) by the elaboration of respective conceptual models. The example of conceptual model for one site with the identification index "CH-Slobozia Mare – 03" in inventory database is presented in this publication (figure 2). The detail investigation included following steps: desk-top study of existing materials about this site for sampling plan elaboration; field study and sampling; determination of toxic substances; risk analysis; elaboration of recommendation for remediation and minimization of existing risks.

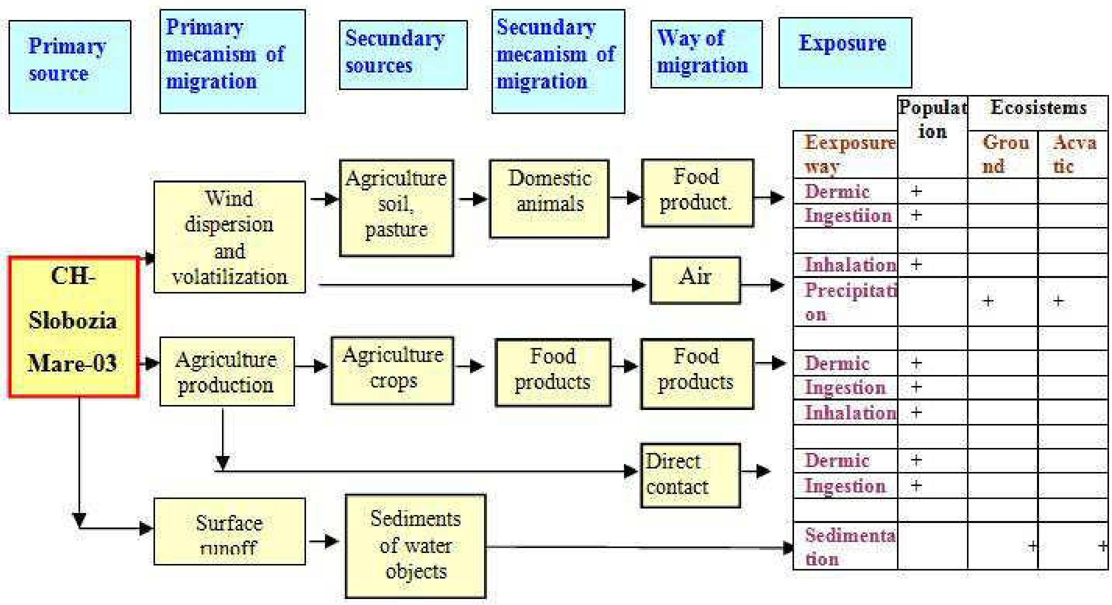

Fig. 2. Conceptual model for local risk assessment of POPs contaminated site CH-Slobozia Mare-03.

This site is agriculture land at present where in the past was a pesticide storage. The sampling plan and general results are presented in figure 3. All territory was separated at 14 lots with different impact from this site.

Fig. 3. Sampling plan and average POPs concentration in soil.

The incremental sampling approach was used for the study of POPs concentration in every lot. The average value shoved a high pollution level for one lot, moderate pollution level for six lots, small pollution for two lots and admissible pollution for next 5 lots. Three executed boreholes with depth 1,0 m shoved the thickness of pollution soil near 0,3 m (arable layer). The polluted soil for lot with high pollution is collected in heap with the high near 1,0 m. Approximate volumes of soil with different pollution is presented in table 6.

Tab. 6. Volume of soil with different pollution calculated by lots

Nr	POPs concentration, mg/kg	Supface, m^2	Volume, m^3
1	12,75	1140	1140
2	6,54	1642	493
3	2,05	1522	457
4	1,42	959	288
5	1,18	1112	334
6	1,15	4363	1309
7	0,59	1462	439
8	0,55	5969	1791
9	0,39	4363	1309

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UPDATE OF THE METHODOLOGY FOR RASTER DATA INTERPRETATION (REMOTE SENSING) FOR DETECTING CLUES OF CONTAMINATION WITHIN THE CONTAMINATED SITES INVENTORY PROJECT

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KEYWORDS
Contaminated sites, inventory, methodology, remote sensing, DTM (Digital Terrain Model), shaded relief

ABSTRACT

A basis of the interpretation methodology of raster data for the purpose of detecting clues of contamination using remote sensing methods is described in the methodology, which is one of the outcomes of the 1st phase of the National Inventory of Contaminated Sites project (NIKM) (Doubrava et al., 2011).
For the second phase of the NIKM project (Suchánek, 2013), prepared for the Operational Programme of the Environment (OPE 2014-2020) (OPŽP, 2013), in order to obtain an optimum number of clues of contamination, we first of all added methodology with the stage of reinterpretation (revision of the clues identified by the first interpreter through the revision of a supervisor).
The aim of this change is to achieve only about 60% of the number of clues interpreted in terms of area (e.g. km^2) in test areas of the NIKM first stage. Given that the methodology NIKM prescribes a mandatory visit and in-situ observation of any evidence of contamination obtained within the project (the output of remote sensing), this reduction of the number of visits has a direct impact (lowering) on the cost of the inventory.
The second methodology supplement consists in the use of the information contained in the Hill Shaded Digital Terrain Model of the Czech Republic of the 4th and 5th generation (DMR 4G, DMR5G),provided by the Czech Office for Surveying, Mapping and Cadastre (ČÚZK) in the form of web services (ČÚZK, 2016a, 2016b). Already this basis alone allows us to find the artificial formations which may indicate (and sometimes clearly indicate) the existence of contaminated sites as they are understood in the context of the NIKM project.
The third update element consists of the systematic use of attributes for objects contained in geographic maps.

RASTER PLATFORM FOR NIKM AND ITS UPDATES

To support the NIKM project, a set of products, technical and organizational measures was, inter alia, created, which together comprised the geographic support of the project activities. The aim was to achieve an accurate spatial localization of found objects of interest and to gather image documentation.
The geographic background documents also contain a variety of other factual data necessary to solve project tasks (field conditions, spatial and logical relations of findings and of their surrounding areas, etc.). From the beginning, the aim is to deliver all this supporting information to all levels of the project, i.e. from the project management up to individual field workers, and, from the tools for managing the project activities to the geographical and other information support for field groups examining the findings in-situ.
The technical means to provide this support are common server database technologies, providing data and maps using WMS (Web Map Service). Software tools comprise tailor made applications for servers and individual clients.
Equally important tools, such as is information technology, are also suitable geographic data. Their selection was chosen so that users can get validated background information that best displays all the necessary information. By using it, a user could accurately locate and properly classify any found clues that are the basis for updating the National Database of Contaminated Sites.
In the pilot phase of the project NIKM I a mapping service was thus created, aiming to meet the needs of project management and of technical specialists. During the project performance a practical experience with use of mapping services was systematically gathered.

The set of data mapping services used in the NIKM I project:

- A photomap from the 1930's - seamless database orthorectified (i.e. exactly geometrically corrected) aerial images with resolution 1x1m. Unfortunately, there is an incomplete coverage (about 50% of the territory of the Czech Republic, part of the original images lost during the war).

- A photomap from the 1950's - aerial photomap for whose creation images of nationwide aerial photography in the1950's(the median is in 1953), were used. There is alack of coverage in some areas, which has been completed with the nearest, in time other available aerial images.

- Current aerial photomap ČÚZK - shows the current status of the Czech Republic. It serves as a reference base for the historical photomap.

- Comparative image layers (binary rasters with contours, generated by filtration of the original orthophotomap) serve for overlapping of the photomap with a strongly simplified real image of another photomap of the same territory. The upper layer contains only the contour line and areal objects; the rest of the layer is completely transparent. This enables us to see, very well, the time changes that occurred in the period between the taking of the older and newer images.

- Landsat ETM - multispectral images from a known NASA satellite. They can be used to colour highlighting the aerial photomap, or to make the spectral analysis of the area and to show the delimitation of the contamination plume, if it’s spectral manifestationscan be found in the image. The test areas, unfortunately, did not contain any extremely contaminated area where it would be possible to test the demarcation of an affected area or to search for specific contaminated surfaces.

- RETM (Raster Equivalent of Geographic Maps) - a set of military maps in the latest available version, shown in raster format and available from web services. It is particularly suitable for obtaining valuable thematic information related to the subject of the inventory (e.g. landfills including their basic proportions, types of industry, the sources of drinking water, etc.).

- Different map layers represented in various combinations prepared in order to identify as many of the events already in preparation in cameral conditions.

- The success rate (a share of clues resulting in the records of potentially contaminated sites) varies between 5 % and15 % of the original number of gathered clues, according to the character of the area and the state of the content of the database.

EXPERIENCE FROM THE NIKM PROJECT FIRST STAGE

Evaluation of raster background data using the methods of remote sensing (RS) was performed in 2009-2013 on 9.4% of the Czech Republic’s area (7397 km^2). 284 clues were identified, from which, after examination, 78 were registered as a contaminated site - see Table 1 (data source: Suchánek et al., 2013).

Tab. 1. Overview of pilot inventory outputs performed in the NIKM project first stage

Features of sites (objects of interest) sets	Number of sites	%	%
Total number of objects of interest gathered from Remote Sensing (historical and current photomaps) and from existing databases - input data set forinventory	8 637	100	
thereofsites, entered into evidence and earmarked forfurther evaluation	284	3.3	100
thereofsites detected using remote sensing	78	-	25.5

Positive experience and results:

- Got a basic overview of the project objects of interest before the start of proper field works.
- Creation of a working background documentation that contains and displays a spatial localization of clues of contaminated sites and illustrates the status of the territory in several historical periods and from different perspectives.
- Developed a planning basis for the management of inventory works.
- Facilitation of the task of field workers, offering them background information for discussion with local authorities etc.
- Significant streamlining of the field works. Field specialists could easily prepare a work plan and optimise logistics (transport, accommodation).

- Documentation of the status of objects of interest (clues, sites) for future use.

Negative experience:

- High complexity in the preparation of certain documents.
- Historical photomap of the1930's does not have nationwide coverage and a number of clues displayed on them is considerably low, and almost exactly overlap with clues and findings on the photomap made from images dated from the1950's.

CURRENT AND NEAR FUTURE STATUS

Based on the above noticed experience, and given the current real possibilities in data security, a portfolio of geographical background documents was partly adapted to meet all the positive achievements of the pilot phase and, where possible, to make use of the newly available options. The following items are in play:

- The photomap of the 1930's will not be included in the background portfolio because of low yields and lack of funds for its creation.
- The photomap of the1950's will be utilized in full.
- Current aerial photomap (ČÚZK) will be used in full.
- Comparative image layer will not be created, instead of that, the transparent maps or other comparative analyses will be used to comparative use.
- Landsat data will not be included in the standard portfolio of documents, but for a more sophisticated ad hoc analyse, newer Landsat 8 data will be considered.
- Texts (attributes, abbreviations) identifying objects and contained in topographic works will be utilized.
- Creation of a type shape catalogue of objects of interest.

New layers

- Sentinel 1 - showing radar data (Synthetic Aperture Radar - SAR) to identify the elements of infrastructure and water areas.
- Sentinel 2 - a new multispectral instrument, comparable to Landsat but having a greater spectral resolution.
- DMR4G and DMR5G - newly acquired altimetric data from ČÚZK, taken by laser altimetry methodology (see Dušánek, 2011)

Sentinel satellites data are available for eventual use, as well as Landsat data. The altimetric data that are available as WMS shaded relief represent a fundamental improvement. Thanks to the highly detailed measurements of the altitudes, "shadowed" formations that reveal surface human activity stand up from the relief model showing these formations in a form of detailed "3rd dimension".

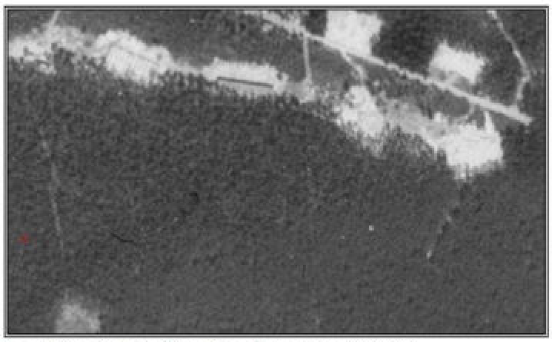
In this paper, we focus on the use of laser altimetry for the inventory of contaminated sites. For the purposes of the NIKM 2 project, the following type of objects can be distinguished:

- Landfills, waste dumps or mine tailings
- Buried terrain depression
- Buried water streams
- Discharge hoppers
- Rock quarries, sand quarries, clay quarries, brickyards, small local quarries
- Underground mines (surface objects and traces of mining activities on the ground, e.g. mouth of a gallery or depressions)

In Figure 1 there is an example of a clue, of a contaminated sites interpretation, using "classical" interpretation of ortophotomaps compared with the image of these objects in a shaded model DMR5G.
The investigated object is situated on the southern edge of an already registered contaminated site - former military base of the Soviet Army in Stráž pod Ralskem (ID56466001 database SEKM). South of the site of former garages of the tank regiment we have identified a rectangular area with dimensions of 60x90 m with coordinates of the centre of the area of 50° 41'46.45 "N, 14° 49'50.27" E. This area is nowadays covered with grown forest and is not mentioned in the current description of the registered site. One interpretation could be that this is an area of a former fuel station of unknown localization noticed in the record of the site. Another possibility is that it is an illegal landfill partially remediated. Based on our clue identification we can proceed to field investigation within the framework of a national inventory of contaminated sites.

Location in current photomap (2010)

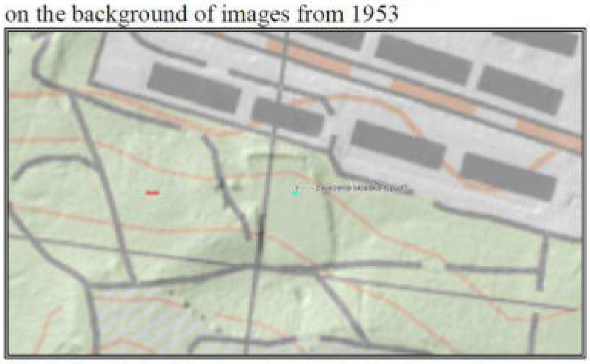
Shaded DMR5G of the location (status quo). Buildings and forest are digitally removed from the model.



Location in the historic photomap (1953)

Shaded DMR5G of the location (status quo) on the background of images from 1953

Shaded model of the location above the photomap from 2010



Shaded model of the location on the background of a topographic map

Fig. 1. Six visualizations of a clue - a new potentially contaminated site close to the site ID 56466001 (Stráž pod Ralskem).

THE ADVANTAGE OF THE USE OF LASER ALTIMETRY

All objects detectable as "strange shapes" on the natural terrain relief are of NIKM 2 interest. They can be found even under vegetation or in other places where from the photomap even from the current map cannot read the actual shape of the terrain. The use of the direct interpretation of the terrain morphology significantly increases the efficiency of interpretation and through it thus supports fieldworks. Omitting this preparation many objects can escape attention when working in the field. Many units can be overlooked due to vegetation cover. The terrain is also not possible to investigate at a reasonable cost at such detail as seen from a bird's eye view. An increase in the number of clues by a third is expected (from about 300 to 400 primary indications). In comparison with the first stage of the NIKMproject, the number of confirmed clues entering in the form of records into the database is expected to increase by 20%.

From the experimentally evaluated territory of five districts, it was found that performing a careful inspection of historical and current photomaps on average about 400 clues could be found in one average district. In the revision step around 150 of the primary clues could be eliminated. Therefore around 250 clues remain as a result from a classic photo-interpretation. In the photomap revision step, the DMR5G is also used as a support to the revision, as well as a tool for finding terrain anomalies that suggest the presence of other clues which cannot be found in the photomap. In this way, approximately 100 of the additional clues are found in the area of one district. In total, out of 350 clues found within Remote Sensing works, roughly 70 % of the clues are detected with photo-interpretation, and 30% with visual analysis of shaded terrain relief. Utilization of DMR5G seems to be a very important and prospective element in the preparation of field investigation.

The success rate of DMR5G utilization for clue searching is demonstrable in an example of the district Chrudim - see Table 2. The situation in four other districts experimentally assessed is similar. The total number of clues varies depending on e.g. character of the district (the rate of industrialization, the rate of land use, population), but the share of clues identified using DMR5G is very similar and stable.

Tab. 2. Share of clues localized using DMR5G on the total number of clues identified by Remote Sensing methods (the case of the District Chrudim)

Clues of the contaminated sites surveyed in two step interpretation and broken down by method (orthophoto vs. DMR5G)		**Number of clues**	**%**	**%**
The number of clues in the district of Chrudim gathered in the first step of interpretation incl. DMR5G		427	100	-
The number of clues discarded with revision (the second step of interpretation)		157	33.4	-
The number of clues in the district of Chrudim after revision		270	-	100
	thereof the number of detected clues gathered within interpretation of orthophotomaps	169	-	62.6
	thereof the number of clues detected using DMR5G	101	-	37.4

VISION

Currently in the Czech Republic we do not have available to us, sophisticated software tools that would allow us to automatically detect clues of contaminated or potentially contaminated sites. Capabilities of useful tools used in geographic information systems and remote sensing are much broader than they are currently used in our country. If there is formulated social demand in this area, we can address particularly the following promising directions:

Advanced terrain analysis (morphology, comparison of slope gradient, edges, heights, different lighting, ...) based on a mathematical analysis of terrain surface formations has not yet been tested. However, in principle it is possible to create algorithms that on the original, so called hydrologically correct shape of the terrain can detect artificially created elevations or depressions. Compared with other background information it is then possible to unambiguously identify the places where it is necessary to carry out another survey of contamination on the surface or just below the surface, and underground (e.g. dumping contaminants in the old mining object), etc.

Hyperspectral image data analysis requires a special sophisticated sensing device which displays Earth's surfaces in a number of very narrow spectral bands simultaneously. Where such data are available, it is possible to purposefully seek certain types of potentially contaminated sites, for which have typical certain specific spectral manifestations of some contaminants or their accompanying components. Such components we call "markants" (characteristic features) and methodology of work with a detailed spectral image can be very precisely focused on their detection of the Earth's surface. This procedure has already been tested in the first stage of the NIKM project. Unfortunately, a widespread use of this procedure is hampered by insufficient spatial resolution (must achieve at least 5x5m or better) and by a total lack of such data.

Comparing older and newer high-quality elevation models is currently the most promising analytical procedure, since at present we already have a relatively good quality of altimetry ZABAGED, which can be compared with DMR4G or DMR5G through map algebra. If technically possible, the NIKM project team provides such a comparison even before the field phase of NIKM II. Based on the comparison, all formations that arose between the period of creation of accurate contour lines and performance of laser altimetry should secede. Filtering out as much of the unnecessarily displayed formations (areas of settlements, new roads, etc.) then will remain for the further processing of the limited amount of detected anomalies that are already appropriate for a detailed interpretation.

An update of methodology through a systematic use of attributes for objects contained in geographicmaps
These attributes (textual data - abbreviated names - of the type of building, plant, installation etc.) bring us relatively useful supporting information, which can lead to exclusion or inclusion of clues of contaminated sites

from or to the list of clues for further investigation. To interpret the clues, the contents of the old raster maps, for example, old maps ZM10 (Base map 1:10 000, Land Survey Office), mine maps, military maps, etc., will also be systematically exploited, namely from the perspective of identification of areas with potential for contamination of soil and groundwater. These include maps showing location e.g. of industrial buildings, farms, mining areas, queries, sand pits etc.

CONCLUSIONS

Based on the activities performed within the 1st phase of the National Inventory of Contaminated Sites project, in view of the 2nd NIKM's phase, the project methodology was completed with the stage of clues reinterpretation, with the use of the information contained in the Hill Shaded Digital Terrain Model, and with the exploitation of attributes for objects contained in topographic works.

In further elaborating of the methodology we will focus on the use of procedures for the routine detection of shapes. The solution would be a synthesis of several partial analyses (terrain morphology, data from GIS, supervised classification of multispectral data, object-oriented classification of hyperspectral images, etc.). The common intersection of these analyses layers will be made and a final clues layer serving for further inventory work - methodical verification of identified contaminated sites – will be elaborated.

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INPLICATION ECOSYSTEM SERVICES IN THE COST OF DAMAGE ASSESSMENT OF RADIOACTIVE CONTAMINATION ON THE EXAMPLE OF FOREST LAND

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KEYWORDS
Radioactive contamination, damage assessment, forest soils, ecosystem services, Chernobyl catastrophe

ABSTRACT

Existing in Russia and Belarus methods of assesement of damage caused by land contamination by chemicals ("Method of determination ..", 1993; "The methodology of calculation ...", 2010) are not capable with the radionuclid pollution due to the specific effect on living organisms . To solve this problem, estimation of costs of reclamation of polluted area and the amount of lost profits should be estimated by the formula (1):
Damage from radionuclid pollution = The costs of reconstruction (reclamation) of lands + Loss of profits (1)

If for determining the cost of reclamation of radioactively contaminated land, the experience of similar studies can be used (Nedotsuk, 2007;. Ratnikov Sapozhnikov et al, 2016), the estimation of lost profits is difficult, since the legal regime of land use, such areas often removed from economic activity. The solution is toexamine and assess ecosystem services - the benefits people obtain from ecosystem - as well as losses of health damages of residents (Groot de RS et al, 2002; Millennium Ecosystem Assessment Ecosystems and Human Well-being: Current. State and Trends Assessment, 2005; Costanza R. et al, 2014) - formula (2):
Damage from radionuclid pollution = The costs of reconstruction (reclamation) of lands + Loss of soil ecosystem services + Losses from health damages of residents (2)

Damage assesement from the radioactive contamination of land for three stationary forest plots located on the territory of the Union State of Russia and Belarus was done. In these areas, each of an area of 2500 m2, for a long time after the Chernobyl catastrophe were carried out monitoring studies.
As a result of measurementwas found that the density of radioactive soil contamination by cesium-137 (137Cs) investigated plots in the Bryansk region and plot in the Gomel region significantly higher than normal (1 Ci / km2) - Tab. 1.

Tab. 1. Results of the plots contaminated with radionuclides analysis

Plot	Radioactive soil contamination density of cesium-137 (137Cs), Ci/km^2		Status of contaminated zone
	Average value of 16 samples	Value in mixed sample	
"1 - Belorussia" (Gomel region)	9,79	7,45	Living area with the right of resettlement (5 - 15 Ci/ km^2)
"1 - Russia" (Bryansk region)	19,40	15,74	Resettlement area (15 - 40 Ci/km^2)
"2 - Russia" (Bryansk region)	14,45	7,29	Living area with the right of resettlement (5 - 15 Ci/km^2)

Measuring equivalent dose rate, taking into account the biological effectiveness of ionizing radiation in 16 points at a height of 3-4 cm and 1 m from the surface of the soil, leed to calculation of the maximum number of working days (Table. 2), as the main limiting factor of forest activities in radioactive polluted areas is a negative impact of increased background radiation on the human body.It should be noted that the minimum allowed value of working time, even on the most radioactively contaminated area (SU-1R) is not less than six months. Considering that the number of working days in a year is 247 (5 day work week), the labor time lost due to the presence of radioactive contamination for the area "1-Belarus" - is missing, for the site "Russia 1" is 64 days, and for plot "Russia-2" - 12 days.

Tab. 2. Dose measurement results at a height of 3-4 cm and 1 m of the soil surface

Plot	The average dose value at a height of 3-4 cm from the soil surface (based on 16 measurements), * 10^{-3} mSv / h	The average dose value at a height of 1m from the surface of soil (based on 16 measurements), *10^{-3} mSv / h	Effective equivalent dose, mSv / year	Permitted number of working days per year
"1 - Belorussia" (Gomel region)	0,55	0,49	4,29	255
"1 - Russia" (Bryansk region)	0,89	0,68	5,96	183
"2-Russia" (Bryansk region)	0,62	0,53	4,64	235

For each of the plots was compiled a list of remediation activities and using SmetaWIZARD program (version 4.0) their costs were determined (Table 3).

Tab. 3. The cost of remediation activities for plots, rub

Activity / cost, rub.	1 – Belarus (Gomel region)	1 – Russia (Bryansk region)	2 –Russia (Bryansk region)
Deforestation	110393,15	84231,11	108559,15
Soil displacement	91638,94	91638,90	91638,94
Recovery of forest vegetation	193933,53	94746,15	119913,10
Total costs, rub./Euro*	395965,62/ 5449,57	270616,16/ 3724,42	320111,19/ 4405,60

*Note: The calculations were carried out in EUR by an exchange rate of the Central Bank of Russian Federation on 25.06.2016

From the total list of ecosystem services provided by the forest ecosystems (Tsvetnov, 2016) (Fig. 1), were allocated especially protecting services, learning and assessment of which is particularly important in conditions of radioactive contamination (Fig. 2). It should be noted that the inclusion of these services is most important while fixing the total economic value of actually or potentially contaminated areas. Because the radiation shielding service does not reduce in case of contamination, it should not be considered as degradation processes in the analysis.Greatest contribution to the cost of the damage is made by direct provisioning services and recreational services.With radioactive contamination it is prohibited to collect certain non-timber forest products (mushrooms), which captures the degradation of providing services, also wood processing, which often found to be clean, requires additional costs, which can be considered as additional parameters of the damage. Speaking about the recreational services, we note that it is not possioble to consider contaminated with radionuclides forest area as a territory suitable for recreation, so the loss of this type of ecosystem services should be included in the assessment of degradation.

The results of the economic interpretation of ecosystem services used in the formula (2), allowed to increase the amount of damage from the radioactive contamination of land, for more than 100%.
Insufficient consideration of ecosystem services loss of soil in assessing the amount of damage from the radioactive contamination of forest areas not only reduces this value, but also distorts the costs of reclamation (recovery) works. Carrying out the complex specified works, including deforestration, removal and disposal of contaminated soil, its replacement with uncontaminated soil, reconstruction of forest vegetation, unfortunately, can not fully compensate caused environmental damages, including a result of migration of radionuclides in the neighboring landscapes.

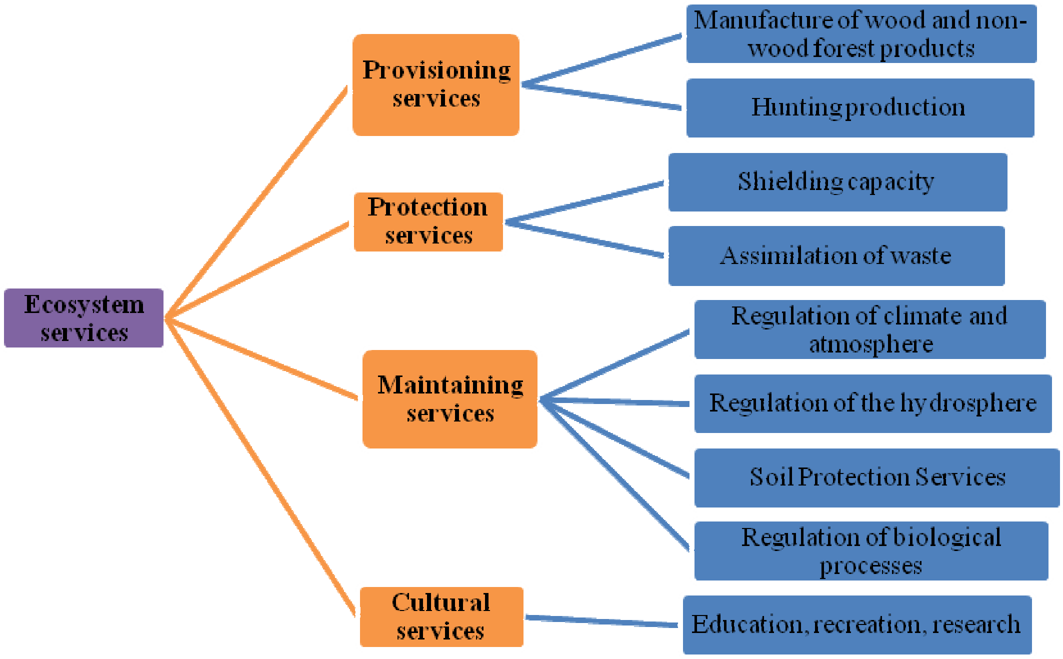

Fig. 1. Total forest ecosystem services biogeocoenose.

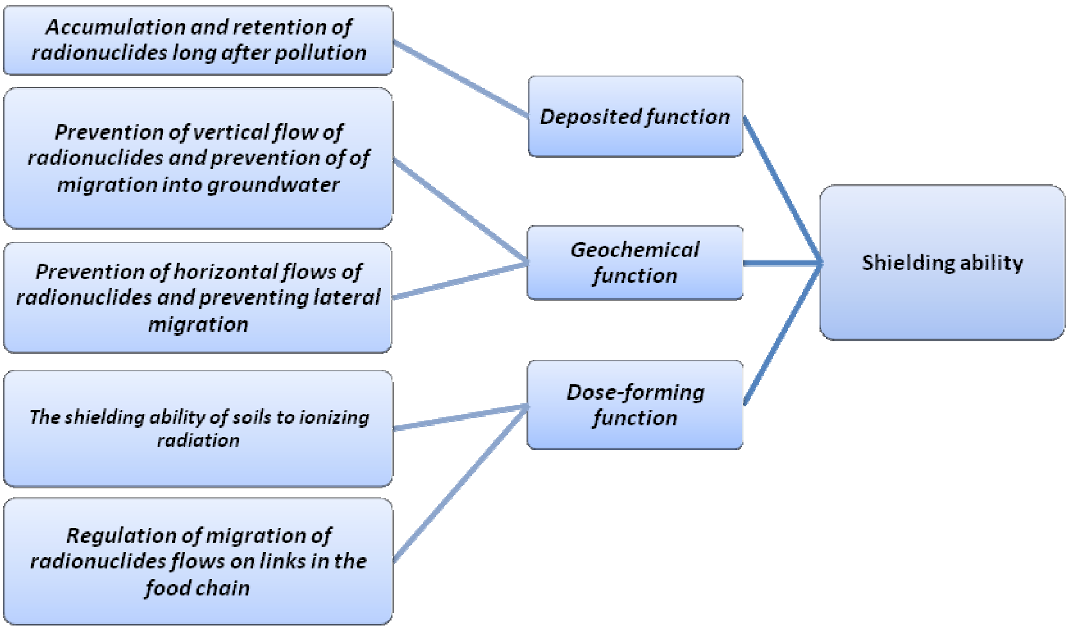

Fig. 2. Soil protecting services related to radioactive contamination.

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APPLICATION OF ENISSA-MIP AS A TOOL FOR HIGH RESOLUTION SITE CHARACTERISATION (HRSC)

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KEYWORDS
High Resolution Site Characterization (HRSC), contamination, chlorinated solvents, DNAPL, soil, groundwater, sampling, in situ analysis, membrane interface probe, GCMS

INTRODUCTION

The success of soil investigations and remediation designs is highly depended on a solid and constantly adjusted conceptual site model (CSM). Underestimation of the contaminated area and or pollutant load can lead to an inadequate remediation design resulting in project failure, budget overshooting and residual risks. A detailed visualization of the contaminant situation will provide the consultant an improved insight in the source, pathways, exposure and remediation alternatives but will also help to recognize and identify the many data gaps and uncertainties.
The CSM is built by collecting data from the site under investigation. The traditional approach is to collect soil samples, send them to a certified lab, and install monitoring wells at the site. About one week later, groundwater samples can be collected from the wells and some days later results are available.The whole process of delineation and mapping of the contamination can become a very intensive and time consuming task. Traditional sampling methods are characterizedlow detection levels and a broad and accurate analysis spectrum but despite the high accuracy and precision of the analysis at the certified labs where the collected samples end up, a large portion of the accuracy is already lost during the sampling, handling and conservation in the field. Environmental consultants are sometimes blindfolded by the final analytical certificate which give them a false sense of certainty. Furthermore the number of data points (samples) is often very low compared to the investigated area and volume.Since hydrogeology and contaminant concentration can vary on a small scale (centimeters), a limited data set can be problematic and will result in a CSM with considerable data gaps, uncertainties and wrong conclusions (see Figure 1). The scale of measurement must be appropriate for the scale of heterogeneity so monitoring wells with typical long screens (meters) are not the optimal investigation tools for pollutant mapping.

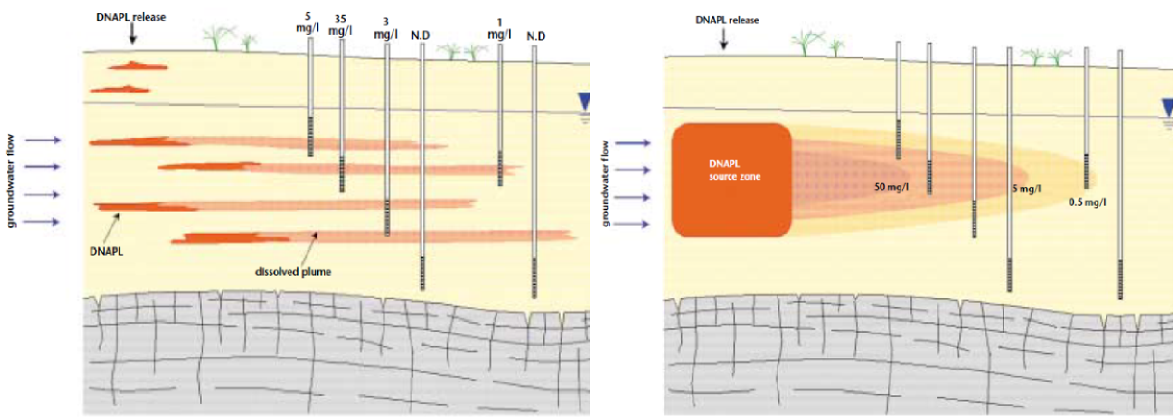

Fig. 1. Cross-section depicting spatial variability of groundwater concentrations in a plume (left). Visual appearance of a smoothly varying distribution of concentration following contouring (right). - Illustrated handbook of DNAPL transport and fate in the subsurface. Environment Agency UK (2003).

Especially for chlorinated solvents (and other dense non aqueous phase liquids (DNAPL) contaminations) which can have very complex occurrence and migration pathways the characterization can be very challenging. In fact a qualitative and cost effective characterization of source and plume zone based on conventional soil samples and monitoring wells alone is very difficult.Additionally, target depths for monitoring wells are often arbitrarilyapprehended for further delineation based on preliminary results, leading to wrong screen depths and an unreliable data.To lower the uncertainty and improve the CSM a higher data density (and more accurate, on-site sampling and analysis methods) should be achieved.

THE MEMBRANE INTERFACE PROBE AND ENISSA-MIP

The conventional MIP is a screening tool with semi-quantitative capabilities to measure volatile organic contaminants (VOC's) in the subsurface, developed by Geoprobe®. Using different push technologies, the MIP is pushed into the soil. The probe has a heated block and a semi-permeable membrane. The block is heated to 120 C° to accelerate diffusion of the contaminants through the membrane. Diffusion occurs because of a concentration gradient between the contaminated soil and the clean carrier gas behind the membrane. A constant gas flow carries the contaminants to the gas phase detector at the surface. For the detection of volatile organic compounds, typically a combination of detectors is used (PID, DELCD, XSD, FID).
In situ screening methods like the MIP are great method to provide a higher data density and perform so called High Resolution Site Characterization (HRSC). In this approach the scale of measurement matches the scale of the contaminant distribution and soil characteristics.
Figure 2 shows different characterization methods and their uncertainty of spatial or analytical nature. Soil and groundwater samples have a low analytical uncertainty due to the high accuracy of the lab analysis, but a high spatial uncertainty arises from their limited number and density. On site investigation methods, such as MIP are frequently used in addition to traditional sampling methods. They are used to provide a screening of semi (volatiles) and make on-site, real time characterization possible. However they are assumed to have a higher analytical uncertainty because of the lower quality of detectors that are usually applied.But due to the high data density the spatial uncertainty is lower.

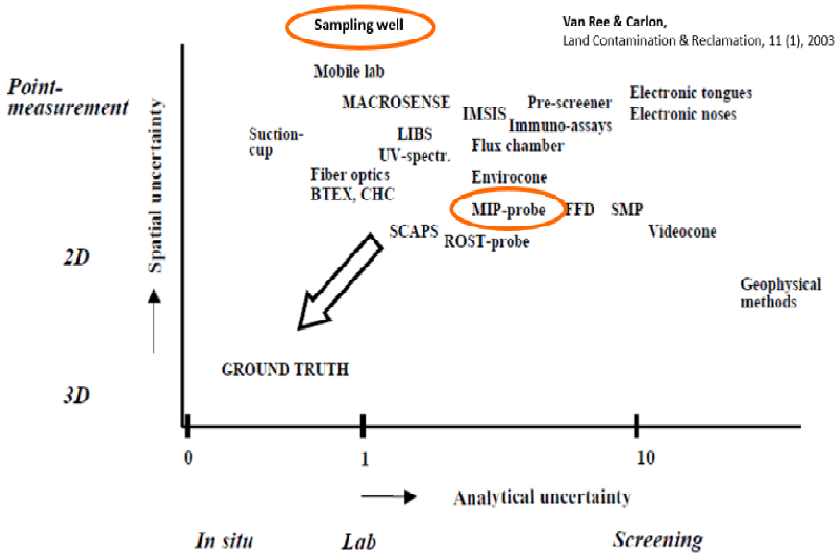

Fig. 2. Sampling methods and the spatial and analytical uncertainty.

Quantification with the conventional MIP however is difficult due to the use of summation detectors. Since the detectors have a different response for different compounds, one cannot correlate the detector signal with concentration since conventional MIP is nondiscriminable. Therefore the conventional MIP system can only give an indication of the order of magnitude of the contaminant concentrations. In addition, the detection limits are much higher compared to for example the remediation standards which are typically risk based. Therefore, conventional MIP is only applicable in the higher concentration zones and not readily applicable for plume investigations. Moreover, for the plume zone, a survey using sampling wells is still needed. This means that for the plume zone, only limited spatial information is obtained. New developments on the detector technology (e.g. XSD) and operation (Low Level MIP) are directed towards lowering detection limits, but intrinsically the detectors remain summation detectors.

The aim of the EnISSA-MIP is to find a better balance between analytical uncertainty and spatial uncertainty by bringing high quality lab detectors to the field. To increase sensitivity and selectivity of the conventional MIP system, the EnISSA method uses a modified GCMS system which is connected to the MIP. The advantages of using a GCMS detector, are the low intrinsic detection limits of the detector and the capabilities to measure individual compounds. Field evaluations demonstrated that the EnISSA MIP is capable of measuring soil profiles for individual compounds with detection limits near 10-20 µg/l.
Since individual components are measured below the soil remediation standards, the applicability of the membrane interphase probe hassubstantially increased. Both source and plume delineation are possible.

Thecomponent specific soil profiles allow reliable “on site” decisions and a dynamic sampling strategy. The on-site information on pollutant cocktails is directly correlated to the remediation standardsand are an added value to the data obtained by the sum-detectors used in conventional MIP.
A typical EnISSA-MIP profile demonstrating the added value of the compound specific results is shown in Figure 3. PCE is degraded to TCE and cis-1,2-DCE but no further degradation is observed and vinyl chloride is not detected.This results indicate the differences in occurrence of the daughter products with depth resulting in more insight in degradation and remedial potential.

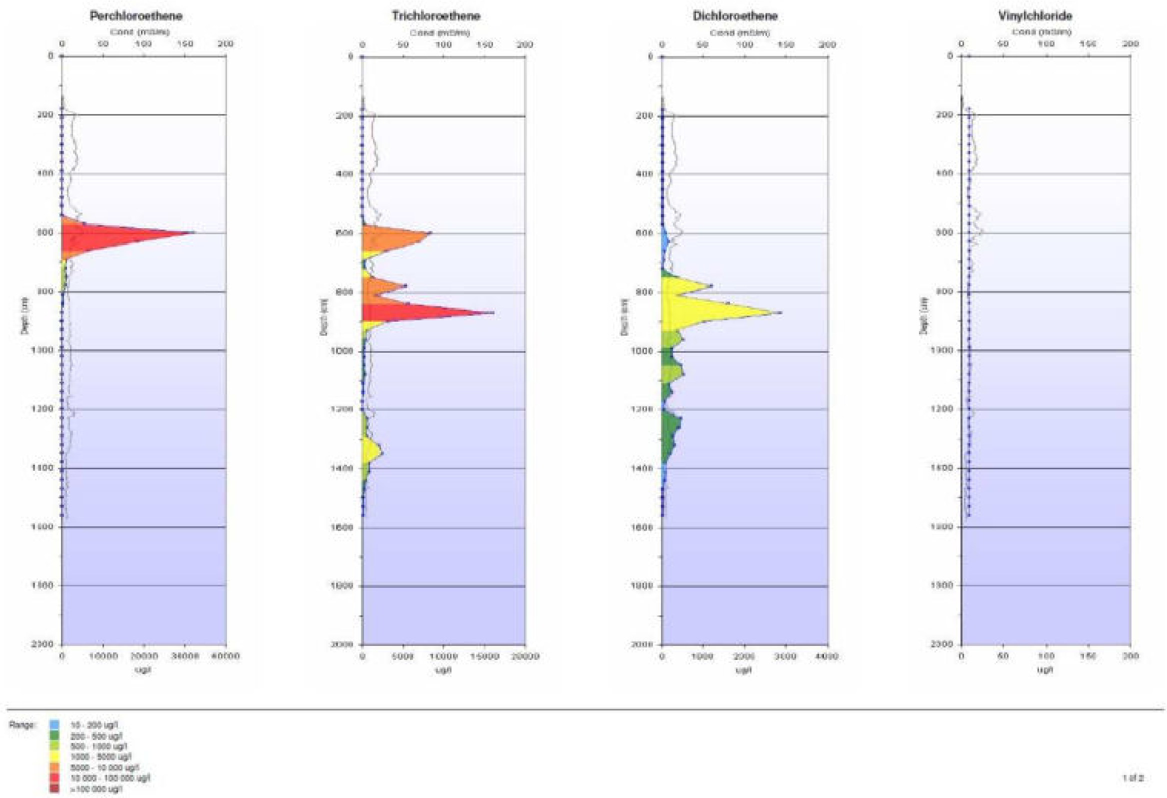

Fig. 3. Typical EnISSA MIP profile with PCE and degradation compounds.

Besides the membrane for the contaminant characterization, the MIP system can be equipped with other soil characterization tools. The electrical conductivity (mS/m) can be used to log particle size of the soil. Sand-sized particles are generally nonconductive and will result in low EC results. Clay-sized particles, tend to be highly conductive due to their extremely small size, relatively high surface area per unit/volume, and charge characteristics so higher EC values generally reflect fine-grained material, whereas lower values indicate coarser sediments.

The combined MIP-CPT probe can measure cone resistance and local friction together with the standard EnISSA-MIP parameters. This type of probes is pushed into the soil at constant speed without hammering by a 20 ton push truck or an anchored direct push rig. Typically, the cone resistance is high in sands and low in clays, and the friction is low in sands and high in clays. Based on the CPT measurements, soils can be classified in 12 categories (Robbertson 1986).

Alternatively a MIP probe with an additional Hydraulic Profiling Tool (HPT) can be used to screen for variations in permeability. This tool uses a water pump to inject a constant water flow in the subsurfaceand pressure transducer to measure the required pressure to maintain the flow. The injection pressure is an indication of the local permeability of the soil. A real-time detailed pressure and flow log is generated for each probing location giving more insight in hydrogeology. Combined with dissipation tests or groundwater level data, an Estimated conductivity (K [m/day]) can be calculated based on an empirical model.
Since 2010 EnISSA has been deployed at more than 150 project locations for different clients throughout Europe (Belgium, The Netherlands, Denmark, Sweden, Germany, France, Spain, Switzerland,…) Those projects showed the benefits of EnISSA in very different contaminant situations going from classicalcVOC’s and BTEX up to MTBE or MIBK, hexane, chlorobenzene, naphthalene…and demonstrated how EnISSA is capable of enhancing the conceptual site model (CSM) resulting in accurate decision making.

CONCLUSIONS

The EnISSA MIP improves the conceptual site model. As was demonstrated bythe comparison between EnISSA and traditional sampling strategies, the EnISSAMIP gives an optimal balance between a low spatial uncertainty and a low analyticaluncertainty yielding a high resolution CSM.
The EnISSA MIP uses an innovative GCMS system which is adapted to connectwith the Membrane Interface Probe (MIP). This connection generates a MIPapplication with component specific detection at much lower detection limitscompared to conventional MIP. This is a major advantage compared to other on site technologies, which in most cases measure sum-parameters.
As was demonstrated on the pilot site, the comparison between the EnISSA MIPand traditional sampling strategies, both in source and plume zone, showed that theresults were in the same order of magnitude (factor 3) as the groundwater samples.This indicates that the EnISSA MIP can be seen as a quasi-quantitative technique forcharacterization of volatile subsurface compounds.
The use of EnISSA during site characterization leads to a cost saving ofapproximately 30 % compared to traditional approaches. Secondly, the cost perscreened meter ("information meter") is much higher for a traditional survey. For asurvey based on the EnISSA MIP, the costs per information meter is about 4 times lower compared to a traditional survey.

All this leads to a higher Return on Investigation (ROI).

EXPLOSIVE ZONE (EX-1) GROUNDWATER REMEDIATION: MONITORING, CONTROL, AND SAFETY MANAGEMENT

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KEYWORDS
In situ chemical oxidation, Enhanced Natural Attenuation, explosive zone (EX-1), *real time* monitoring, BTEX, real-time qPCR.

SUMMARY

Difficulty of remediation projects in Central Europe has been rapidly increasing throughout the past two decades, either because of natural background complexity, or due to complicated anthropogenic conditions. This paper describes pilot deployment of *in situ* chemical oxidation (ISCO; using Modified Fenton's Reagent – MFR) and enhanced natural attenuation (ENA) for the remediation of a BTEX-polluted site located at active petrochemical facility. Together with technology verification, the study tested possible ways of *real time* reaction control and project safety management at the edge of explosive zone (EX-1). Monitored risk-factors included exothermic reaction character, corrosiveness of reagent and groundwater level (against present industrial utility networks), and generation of volatile organic compounds (VOCs). Effect of ENA (nutrient and terminal electron acceptor (TEA) supplement to the target zone after the ISCO application) on ambient microbial communities was also evaluated using a short term injection test and methods of molecular microbiology (based on Polymerase Chain Reaction – PCR). Aside from successful site remediation, we provide an insight on useful tools for reaction and safety management control using standard as well as advanced monitoring techniques.

INTRODUCTION

Recent political development emphasizes cost- and time-effectiveness of all environmental remediations proposed in Central Europe. Moreover, focus of later remediation projects has shifted towards more *difficult-to-treat* sites, in contrast to 1990s and early 2000s. Quicker and more intense technologies are deployed in order to feasibly reach specified contamination limits, commonly requiring *in situ* application are often based on chemical, physicochemical, or biochemical processes.

In situ techniques are used to address wide range of contaminants with a broad interval of pollutant concentrations treatable[1]. Infiltration of oxidizing agents into ground, i.e. ISCO, leads to destruction of pollutant either dissolved in groundwater, sorbed on soil matrix, or present as a free phase product[2] and it is used for remediation of wide variety of contaminants[3].

Fenton's Reagent (FR; the mixture of H_2O_2 and Fe^{II}) is a frequently used ISCO oxidant for remediation of petroleum hydrocarbon-contaminated sites. However, several crucial considerations must be kept in mind when using FR: 1) FR is highly instable with exothermic decomposition releasing large volumes of O_2; 2) in reaction with organic contaminants, FR can produce high amounts of VOCs posing a significant threat to operation health and safety protocol; and 3) potential corrosiveness of FR. Various stabilizing modifications have been devised for the FR in order to keep the reacting iron in dissolved state[4] – mostly by lowering solution pH, which in turn increases its corrosiveness to any subsurface constructions (e.g., building foundations or utility networks).

Molecular microbiology methods (real-time qPCR, fluorescent microscopy) provide vital tool to study environmental microbial communities without any cultivation bias. Specifically, time-variation in relative quantities of genes coding for denitrification enzymes is commonly used to study presence of denitrifying metabolism within ambient microbial communities[5].

The site is located inside fully operational petrochemical plant Unipetrol RPA, ltd. (Litvinov, Czech Republic) and it covers the area of 530 m^2. Major pollutants of interest are BTEX (benzene, toluene, ethylbenzene, and xylenes), naphthalene, and NOC (nonpolar organic compounds). The target unconfined sandy-gravel aquifer is

about 3 m thick with estimated porosity of 0.15 and it is underlaid by isolating clays at depth of 5 m bgs (below ground surface). The contaminated groundwater table reaches 2-3 m bgs with groundwater flow generally in the NE–SW direction and average hydraulic conductivity $K = 2.6 \times 10^{-4}\ ms^{-1}$.
Main objectives of the study were 1) to verify functionality and usability of the technology in target site conditions, 2) to reach set contamination limits, 3) to avoid compromising the rigorous safety regulations of the immediately adjacent EX-1 zone, 4) to define and optimize techniques for on site monitoring, evaluation, and control of oxidation processes (*real time* monitoring), and 5) to evaluate response of ambient microbial communities to EA. Investigated risk-factors included 1) exothermic course of oxidation 2) reagent corrosiveness (MFR stabilization with citric acid – a requirement to maintain groundwater pH ≥ 4.5 and groundwater table below subsurface constructions (utility networks), and 3) VOCs generation.

METHODS

Project design. Total of seven application events was carried out between Nov-13-2013 and Jan-28-2014, injecting 77 m^3 of 5 % (w/v) MFR (stabilized by citric acid). Complete situation of pilot-testing field is shown in Figure 1A. To simulate dynamic flow conditions (expected for full scale remediation), groundwater was pumped from well HV-8857 between particular injection events. Pumped water was cleaned on granular activated carbon and recycled back into target zone to increase local hydraulic gradient and to enhance remediation of capillary fringe by flushing. Due to generation of significant amounts of VOCs as oxidation daughter products, venting was used to extract and clean soil air with activated carbon filter. One year after pilot test conclusion, 20 m^3 of nutrient (NH_4^+, PO_4^{3-}) and TEA (NO_3^-) mixture were injected in order to reach the C:N:P ratio of 100:10:1.

Field monitoring. Every MFR application event was on site *real time* monitored for changes in groundwater level and temperature using automatic sensors Levelogger (Solinst, CAN) and for H_2O_2 kinetics using field photometer MD 600 (Lovibond, GER). Along with applications, field measurements of groundwater physicochemical parameters (red-ox (ORP), dissolved oxygen (DO), electric conductivity (EC) and pH) were regularly performed. Concentrations of VOCs in the soil air were regularly monitored using the photoionization detector (PID) MiniRAE3000 (RAE Systems, USA). Environmental DNA was collected from groundwater on sterile micro-filters (mesh = 0.45 µm), transported on ice, and processed within one day of collection.

Laboratory analyses. Pollutant concentrations were regularly analyzed in an accredited laboratory. Response of ambient microbial communities to supplement of nutrients and TEA was investigated by real-time qPCR using primers 16S rDNA targeting the whole 16S subunit of prokaryotic genome and primers nirK and nirS targeting the denitrification genes.

Real time monitoring. An example of automatic groundwater level, temperature, and EC logging performed in application well is shown in Figure 1B. MFR application had an obvious effect: groundwater level rise, temperature drop (mixture preparation in winter conditions), and EC drop (low MFR mineralization). After the initial peak, groundwater table did not exceed the depth of utility networks. Considering conical shape of groundwater table around application well and relatively high hydraulic conductivity, requirement to keep groundwater table below the level of utility networks was undoubtedly fulfilled. Overall increase in groundwater temperature did not exceed 5 °C, which in turn indicated that the EX-1 zone safety regulations were obeyed.

VOC concentrations. Figure 1C shows the development of VOC concentrations on the output of venting filter. Three rising curve segments display lessening slope steepness, which implies increasing filter durability as reaction intensity gradually decreased over time (decreasing pollutant concentrations). Moreover, field monitoring of target zone VOC levels (directly from monitoring probes) provided information on the situation of residual contaminant present in aquifer and thus served as an application targeting tool.

Hydrogen peroxide utilization. Figure 1D shows an example of H_2O_2 degradation kinetics from one of targeted MFR applications. Field measurements revealed the 1st order-like (quasilinear) kinetics of oxidant degradation in aquifer. Such data further aided with MFR application targeting: quicker oxidant degradation pinpointed persistent pollutant presence in monitored area. With time, H_2O_2 degradation slowed down across pilot field indicating decrease in oxidable matter content. Consequently, MFR oxidation zone range increased with active reagent being carried further from injection point with groundwater.

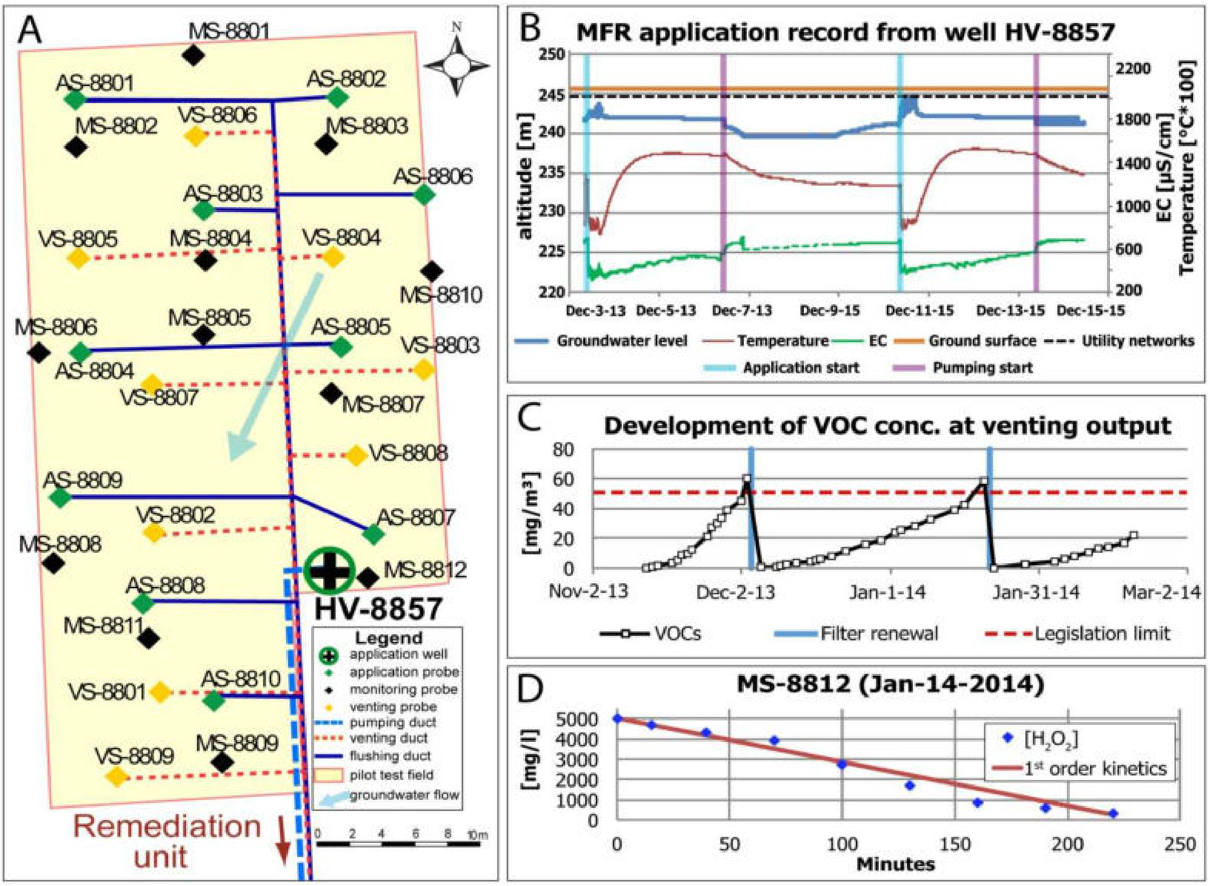

Fig. 1. A, Pilot test field; **B**, Example of *real time* monitoring of groundwater level, temperature, and EC (electric conductivity) between two application events; **C**, Venting system efficiency during the pilot test; **D**, Hydrogen peroxide utilization kinetics example from targeted MFR application.

RESULTS AND DISCUSSION

Physicochemical parameters. Long-term monitoring of pH, ORP, and DO displayed response of environmental conditions upon MFR injection: each of the parameters displayed rapid changes with decreasing intensity with distance from application point and with time. Measured pH was always above the corrosiveness limit (pH = 4.5), throughout the test field (including HV-8857 itself). Hence, it is apparent that both safety regulations addressing the groundwater corrosiveness (groundwater level and pH) were successfully observed. Monitoring of ORP revealed the efficiency of ISCO technology with groundwater red-ox conditions in monitoring probes reaching values up to 400 mV (field data). Elevated ORP tended to drop back after each application and exhibited gradually higher return-values as number of application events rose and amount of remaining oxidable organic matter in the target zone decreased. Along with ORP, DO concentrations increased throughout pilot test field upon MFR injections, regularly reaching values >20 mg/L (instrument detection limit). Observed trend of DO demonstrated direct transformation from anaerobic (before) to aerobic (during) and back to anaerobic (after pilot test) conditions, forcing ambient microbial communities to appropriate shifts in metabolic preferences, benefiting mainly species capable of facultative metabolism (data not shown).

Pollutant concentration. Table 1 displays pollutant concentration history as recorded in the well HV-8857, indicating positive effect of applied ISCO technology. Generalized contamination contour maps are shown in Figure 2, depicting concentrations before and after the pilot study. Concentration gradient slopes generally with respect to direction of local groundwater flow.

Tab. 1. Contamination history in the well HV-8857; ¹ before pilot test, ² after pilot test

CONTAMINANT	Benzene	Naphthalene	NOC
	[μg/L]	[μg/L]	[mg/L]
Concentration limit	2 500	2 500	20
Mar-2004	19 300	276	19
Oct-2006	125 000	<0,5	>200
Nov-2013¹	10 300	162	13,2
Feb-2014²	404	36,8	2,87

Enhanced natural attenuation: Figure 3 shows changes in relative quantity of target denitrification genes (nirK, nirS) in three monitoring probes. While nirS gene exhibited only minimum response to TEA (NO_3^-) supplement, nirK gene showed 10-30 times increase in relative quantity. Consistently with lack of DO after pilot test, this indicated development of nitrate respiration metabolism in ambient microbial communities.

CONCLUSION

The pilot study outcome can be summarized by recapitulation of defined objectives: 1) effectiveness and feasibility of remediation using MFR in target site conditions was confirmed, 2) contamination levels were reduced by several orders of magnitude within two months of application, 3) safety regulations of EX-1 zone were met without reservation, 4) tools for *real time* monitoring and process control were tested and optimized for full-scale application, and 5) potential of ENA application for recovery of ambient microbial communities was observed.

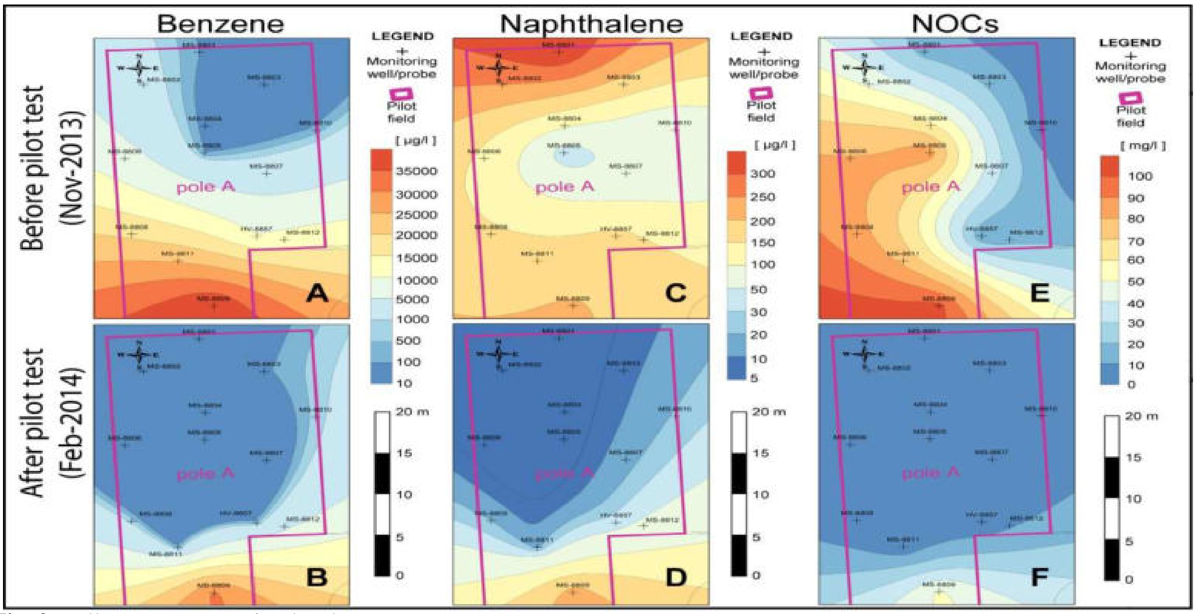

Fig. 2. Pollutant concentration level maps.

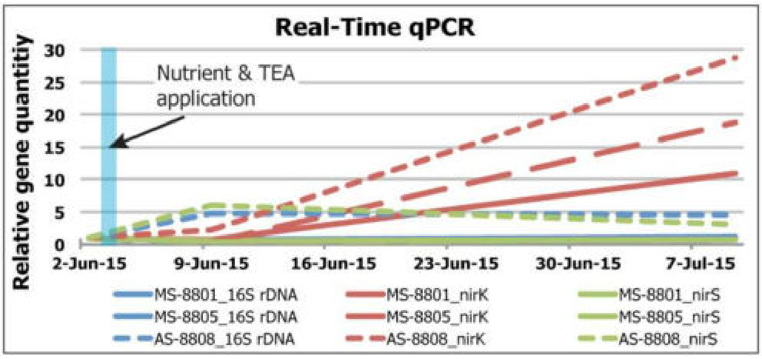

Fig. 3. Changes in relative gene quantity after ENA application.

Study of risk-factors revealed the following findings: 1) groundwater temperature increased less than 5 °C due to exothermic oxidation character, 2) throughout the pilot study, groundwater table remained below the level of local utility networks and the environment maintained pH > 4.5 (corrosiveness limit), and 3) amounts of generated VOCs (ISCO daughter products) decreased over time as intensity of oxidation reactions diminished. Despite strenuous site conditions in the vicinity of EX-1 zone, ISCO technology using MFR proved to be fully feasible for projected remediation.

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DEVELOPMENT OF A HIGH-THROUGHPUT MULTI-PARAMETER BIOMARKER SET FOR PLANT BIOMONITORING AND ECOTOXICOLOGICAL STUDIES

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KEYWORDS
Biomarker, biomonitoring, high-throughput, oxidative stress, plant stress, photosynthesis, secondary metabolism, sugar metabolism

ABSTRACT

During the last decade plants have been increasingly used in ecotoxicological studies and environmental biomonitoring (Walker *et al.*, 2012). In order to evaluate the impact of stress (biotic or abiotic) on plants, it is important to evaluate plant health. This can be realized at the macroscopic scale (growth, number of leaves, dry weight, fresh weight…) or at the molecular scale, using biomarkers. Evaluation of plants health using biomarkers can be relevant especially if numerous biomarkers are combined (Amiard-Triquet et al., 2012). Nowadays, a reduced set of biomarkers is used to determine plant health because some biomarker evaluation methods are costly, time-consuming and have high variability (operator-dependent extraction step).
Thus, the two main limits of the current methods are:
- lack of sensitivity and reliability: the small number of biomarkers does not allow an accurate evaluation of plant health;
- low-throughput: the small number of analyzed samples is not compatible with large scale experiments (i.e. biomonitoring studies).

It appears there is a need to develop an alternative, fast, cost-efficient and reliable high-throughput method able to evaluate plant health in ecotoxicological studies.
The main objectives of our work were to:
- develop high-throughput extraction method;
- develop high-throughput analysis method;
- compare this method with classic methods.

Nowadays, the extraction step is most of the time realized by grinding with a mortar and a pestle. This method is really time-consuming and totally operator dependent. There is a high variability and a really low-throughput. A new method had been developed in the laboratory using bead mill (Fig 1.).

Fig. 1. Comparaison between the three studied extraction methods.

Different parameters were compared in order to obtain the best repeatability and extraction yields. The bead material (ceramic, glass, stainless steel, tungsten carbide...), size (2, 3, 4, 5 and 6 mm) and number of beads (1, 2, 3, 4 and 5) have been tested. Several plate characteristics had also been evaluated: shape (round, square), bottom (conical, flat, round, V-bottom), and volume (1 and 2 mL). The selected method uses one 4 mm glass bead in a 2 mL 96 wells microplate, round-bottom. This high-throughput extraction method allows to grind 186 samples in few minutes.

The second bottleneck limiting biomarker use is throughput analysis. Consequently, most of studies dealing with plant health use a limited biomarker set. The use of cuvette is really time-consuming and totally incompatible with experiments or studies with a lot of samples to analyze (e.g. biomonitoring studies). Nowadays, microplate analysis is more and more used as it is faster and cost-effective (limited volume of reagents). However, most of biomarker protocols have not yet been miniaturized. A part of this development was to miniaturize biomarker protocols.
Usually in plant health evaluation, only few biomarkers assessing oxidative stress (e.g. lipid peroxidation and antioxidant enzymatic activities), and impact on photosynthesis (e.g. chlorophylls a, b and carotenoids contents) are used (Fig. 2).

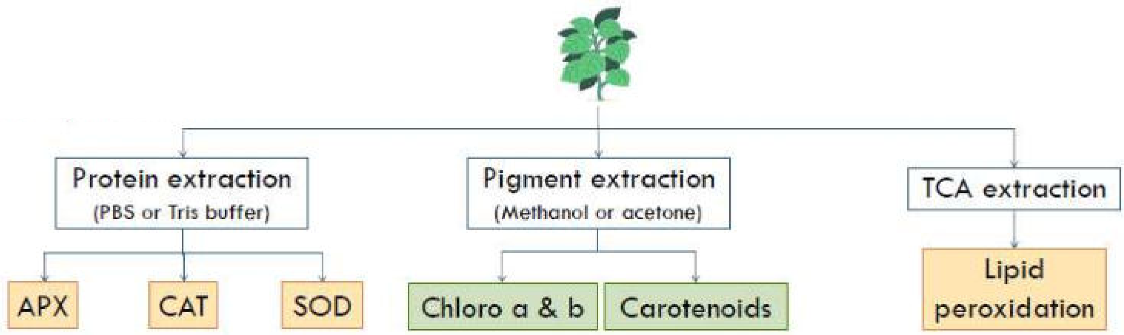

Fig. 2. Biomarker set most commonly used on plants in ecotoxicological studies to evaluate plant health.

However, the use of few biomarkers is not relevant to evaluate accurately plant health. The first step of our work was to determine alternative biomarkers that could be added in our biomarker set. We selected 21 biomarkers to evaluate stress effects on oxidative stress, photosynthesis, secondary metabolism and sugar metabolism. Based on protocols found in the literature, 7 extractions were originally required to analyze these 21 biomarkers (Fig 3).

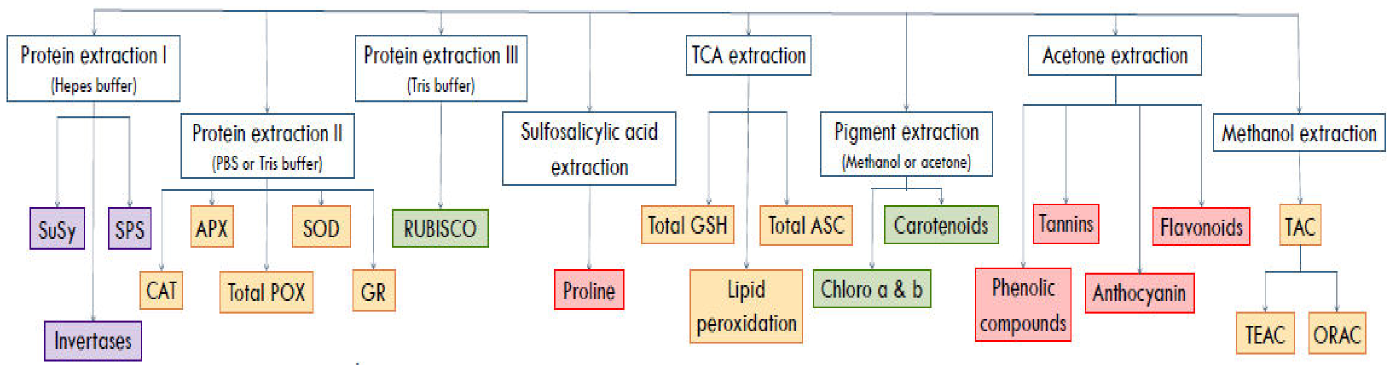

Fig. 3. Proposed set of biomarkers to evaluate plant health without protocol optimization.

Thus, our first goal was to merge several extractions (e.g. the four protein extraction protocols) in order to save time and reduce costs, without reducing assay sensitivity. For each biomarker, several extraction and reaction buffer were tested. Extraction yield and assay repeatability were evaluated in order to have the best buffers. At the end, 3 types of extractions were selected (Fig. 4).

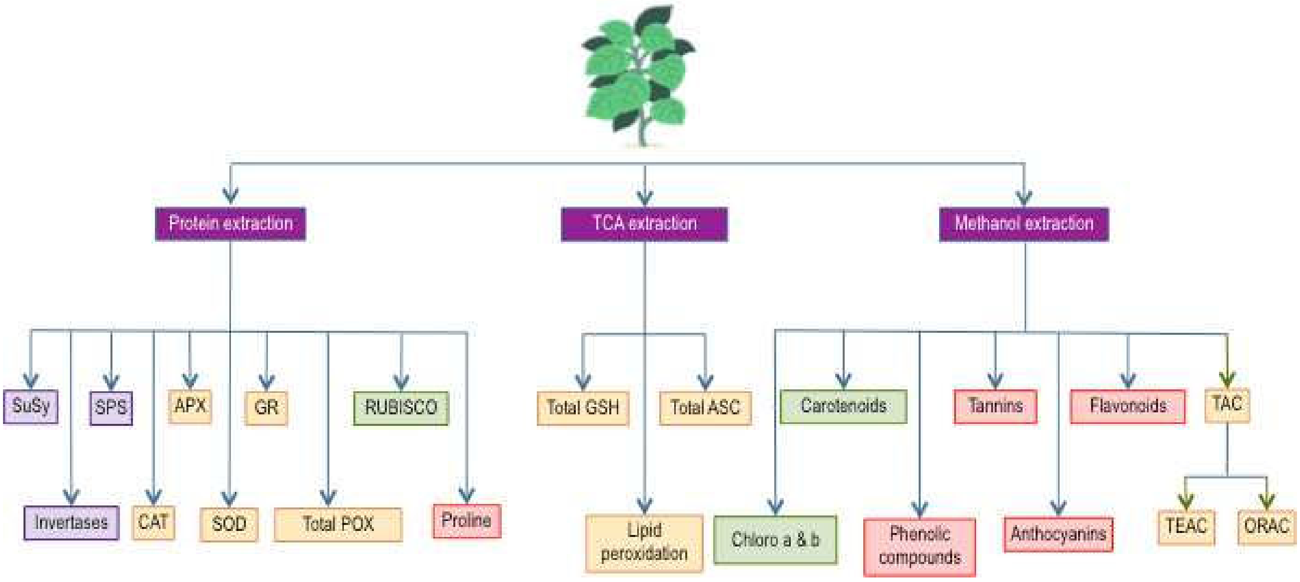

Fig. 4. Proposed set of biomarkers to evaluate plant health with protocol optimization.
Light purple box: sugar metabolism; yellow box: oxidative stress; green box: photosynthesis; pink box: secondary metabolism.

The use of this biomarker set combined with an automatic extraction step (bead mills) presents several advantages (Table 1). The use of bead mill improves extraction step reproducibility and strongly increases its throughput saving several days/weeks of work. The combined use of the optimized set of 21 biomarkers allows to analyze 21 biomarkers on 186 samples in 6 days compared to 45 days (7.5 times faster) required to analyze only 6 biomarkers with the classical method (mortar/pestle and cuvette). This improved protocol also strongly reduces analytical costs and allows to analyze 3 times more biomarkers with a 40% reduced budget.

Tab. 1. Price and time comparison between the different biomarker sets (classical set with 6 biomarkers; 21 biomarkers without protocol optimization and 21 biomarkers with protocol optimization) and analysis methods (mortar/bead mills and cuvette/microplate)

		Mortar and pestle + cuvette	**Mortar and pestle + microplate**	**Beads mill + microplate**
	Grinding	0	0	++
	Analysis	+	++	++
Analytical time (186 samples)	6 biomarkers	45 days	30.5 days	5 days
	21 biomarkers 7 extractions	130 days	76.5 days	13 days
	21 biomarkers 3 extractions	85 days	31 days	**6 days**
Analytical cost (186 samples)	6 biomarkers	570 €	50 €	50 €
	21 biomarkers 7 extractions	9,140 €	500 €	500 €
	21 biomarkers 3 extractions	6,630 €	350 €	**350 €**

In this work, we proposed a new set of biomarkers with a high-throughput method of analysis allowing a better and more accurate evaluation of plant health. This set of biomarkers offers an extended evaluation of oxidative stress (11 biomarkers instead 3-4) and includes the evaluation of secondary metabolites and of enzymes involved in sugar metabolism which could be affected by abiotic and biotic factors. Moreover, this method presents better reproducibility, a higher-throughput and strongly reduces costs.

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REDUCTION, ADSORPTION, AND PRECIPITATION OF HEAVY METALS IN GROUNDWATER BY A REAGENT BASED ON ELEMENTAL IRON, IRON SULPHIDES AND RELATED REACTIVE MINERALS

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KEYWORDS
Metals treatment, Iron chemistry, MetaFix®

SUMMARY

High concentrations of heavy metals are found in many soil and sediment environments. At very high concentrations, heavy metals can be acutely toxic to microorganisms. Treatment approaches that rely on microbial processes may not function well in such acutely toxic environments because processes important to their efficacy, such as carbon fermentation, oxygen consumption, and biological sulfate reduction, can be significantly slowed or even completely inhibited. Hence, in such toxic environments, metals treatment reagents that are not dependent on microbial activity but rather combine reduction with adsorption and precipitation of heavy metals can be advantageous. MetaFix® is an innovation which represents an entirely new family of reagents for treatment of soil, sediment, industrial wastes, and groundwater contaminated with heavy metals. Their treatment mechanisms are based on iron, iron sulfides, and other iron-bearing minerals, and therefore result in heavy metal precipitates that include sulfide and/or iron. These iron/sulfide-bearing heavy metal precipitates generally have lower solubility, and greater pH-stability, than precipitates which do not incorporate iron or sulfides (i.e., heavy metal hydroxides). Performance data showing reductions in leaching of arsenic, mercury, and lead metals will be presented.

INTRODUCTION

The reduction, adsorption, and precipitation of heavy metals by elemental iron, iron sulfides, and related reactive minerals are an emerging science. *In situ* chemical reduction (ISCR) has increasingly been applied to treatment of soil and groundwater contaminated with chlorinated organics. The mechanisms involved in such applications are now fairly well understood and widely recognized in the environmental remediation community. ISCR can be broadly defined as a category of *in situ* soil and groundwater remediation technologies in which treatment occurs primarily by chemical reduction of contaminants, mediated mainly by abiotic processes. It is also recognized that ISCR mechanisms of contaminant reduction can be stimulated by microbial activity (e.g., carbon fermentation), and even created solely by the activity of microorganisms (e.g., biogenic reactive minerals). The major groups of reductants operative in ISCR treatment of soil and groundwater can be broken into four categories, including (a) elemental iron such as ZVI powder, (b) minerals that derive their reducing power from Fe^{+2} such as magnetite and ferruginous clays, (c) minerals that derive their reducing power from reduced S^{-} or S^{-2} either alone or in combination with Fe^{+2} such as pyrite, and (d) organic matter containing redox-active functional groups. All the mechanims involved in ISCR degradation of chlorinated organics are now understood to be related to the transfer of electrons from a reducing agent (the electron donor) to an oxidized species (the electron acceptor). The same cannot, however, be said for the application of ISCR to treatment of heavy metals. In fact, at very high concentrations, heavy metals can be acutely toxic to microorganisms. Treatment approaches that rely on microbial processes may not function well in such acutely toxic environments because processes important to their efficacy, such as carbon fermentation, oxygen consumption, and biological sulfate reduction, can be significantly slowed or even completely inhibited. Hence, in such toxic environments, metals treatment reagents that are not dependent on microbial activity but rather combine reduction with adsorption and precipitation of heavy metals can be advantageous.

Therefore, the new reagents are composed of mixtures of reducing agents (ZVI, iron sulfides), processed reactive minerals (iron oxides, iron oxyhydroxides), pH modifiers, silicates, and catalysts. This new approach is insensitive to toxicity, and performs well even in environments that have high metals concentrations, high concentrations of organic contaminants such as chlorinated solvents, high salt content, or pH levels (high or low) that would inhibit carbon fermentation and sulfate reduction. Another unique advantage of these reagents is their ability to simultaneously treat heavy metals and chlorinated solvents. *In situ* reactive zones can be constructed to prevent migration of heavy metals into sediments or surface water.

DISCUSSION OF MECHANISMS TO TREAT ARSENIC

A main mechanism of arsenic mobilization in soil or groundwater treated with MetaFix is reduction of adsorbed arsenate [As(V)] anions to arsenite [As(III)]. The reduction step is mediated by two of the main components of MetaFix (i.e., ZVI and iron sulfides). Since arsenite occurs as an uncharged $As(OH)_3$ species in the natural pH range, its desorption follows the reduction step and the dissolved arsenic concentration increases. Treatment of dissolved metals such as arsenic in material treated with MetaFix zone involves their long-term sequestration as solid arsenic species by means of reductive precipitation and adsorption onto the surfaces of iron oxides, iron oxyhydroxides and other iron corrosion products. The primary mechanism of removal involves precipitation of arsenic with iron and other inorganic compounds - especially those associated with sulphide – to form mixed iron-arsenic solid phases such as arsenopyrite (Craw *et al*., 2003; Manning *et al*, 2002). Dissolved arsenic is thereby transferred from the aqueous phase to a highly insoluble solid phase (i.e. immobilized).

Creation of reducing conditions is part of the processes leading to arsenic treatment with MetaFix. Both ZVI and iron sulfides are powerful reductants (electron donors), as presented in the following redox half-reactions:

ZVI Corrosion (oxidation): $Fe^0 \rightarrow Fe^{2+} + 2e^-$
Iron Sulfide Oxidation: $FeS \rightarrow Fe^{2+} + HS^-$

These processes provide free ferrous iron and electrons and subsequently produce stable As-Fe sulfide phases. Corrosion (oxidation) of solid ZVI particles produces dissolved iron and subsequently secondary iron minerals are formed, such as iron oxides [*e.g.;* magnetite, Fe_3O_4) and iron oxy-hydroxides (goethite, FeOOH)]. These mineral phases provide reactive surface areas where arsenic oxyanions [As(V) and As(III)] can be bound or co-precipitated (Manning *et al.,* 2002; Kober *et al*., 2005). Similarly, oxidation of solid FeS provides free iron (Fe^{+2}) and sulfide to react with As(III) resulting in precipitation of insoluble iron-As-S phases including arsenopyrite.

MetaFix reagents are designed to have near neutral pH and therefore do not affect soil or groundwater pH. Therefore, geochemical conditions created in the soil, sediment, or groundwater under MetaFix treatment (*i.e.* low Eh and neutral pH) are conducive to the creation of secondary iron minerals, such as goethite and magnetite and As-S species (**Figure 1**).

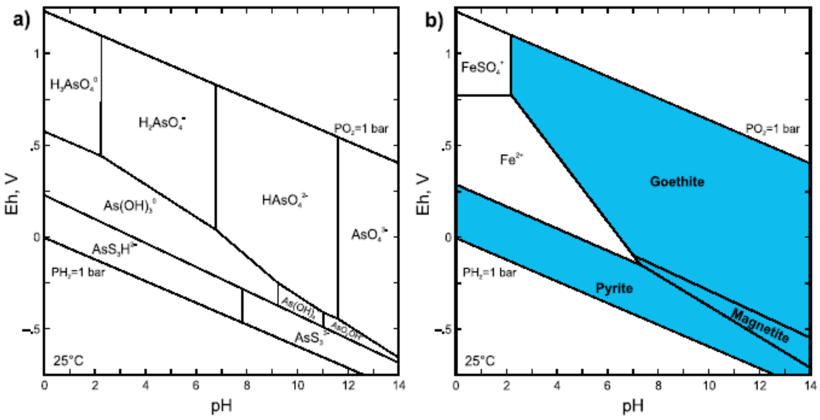

Fig. 1. Eh-pH diagrams for arsenic and iron at 25°C for coupled iron- and sulfate-reducing systems. These paired diagrams show the relative distribution of potentially adsorbing arsenic species (left) relative to representative types of Fe-bearing sorbents (right) that are predicted to occur as a function of Eh and pH.(a) System As-S-H_2O, with $\Sigma As=10^{-5}$ and $\Sigma S=10^{-3}$; all solids suppressed to show stability fields for the aqueous species. (b) System Fe-C-S-H_2O with ΣFe=10-4, $\Sigma C=10^{-3}$, and $\Sigma S=10^{-3}$; Hematite is suppressed (From EPA, 2007).

LONG TERM STABILITY OF IRON-ARSENIC-SULFIDE SOLID PHASES

Considering the continuous source of dissolved iron in the presence of ZVI and FeS and the overlapping stability field of pyrite (FeS) and AsS species, arsenopyrite (FeAsS) is the major solid arsenic phase created during

MetaFix treatment. Arsenopyrite is extremely insoluble under reducing conditions (Eh<0 mV), but it is highly soluble in oxic conditions (Craw *et al.*, 2003):

$$FeAsS + 7H_2O \rightarrow Fe^{2+}_{(aq)} + H_3AsO_{3(aq)} + 11H^+ + 11e^- + SO_4^{2-}$$

The creation of Fe-As-S phases was demonstrated experimentally in iron + sulfide treated soil columns (Przepiora *et al.,* 2008). These results showed that a significant part of the arsenic mass immobilized in the soil was associated with secondary iron oxides and oxyhydroxides, which is in agreement with previous published results in iron rich systems (Manning *et al.*, 2003 Koeber *et al.*, 2005). These solid arsenic species are highly stable. Long-term data showed that the ferrous iron created in the treated soil prevents arsenic remobilization by:

- **Creating protective coatings on the precipitated reduced arsenic mineral phases; and**
- **Facilitating precipitation and/or adsorption of any arsenic that is potentially mobilized under extreme changes in geochemical conditions**

Tab. 1. Summary of the potential arsenic mobilization processes in natural environments and the corresponding anticipated MetaFix treatment mechanisms that prevent arsenic remobilization

Attenuation Processes*	Mobilization Processes*	Anticipated MetaFix Mechanisms
Precipitation of metal arsenates or arsenites or precipitation of arsenic sulfides	Dissolution of metal arsenates/ arsenites due to change in pH; dissolution of arsenic sulfides due to increase in pH or shift from reducing to oxidizing conditions.	MetaFix is a pH neutral reagent , therefore pH is maintained ay levels below zero point charge (ZPC) of iron oxides and oxyhydroxides (<8). MetaFix treatment provides a long term source of free iron from oxidation of ZVI and FeS. This enables continuous formation of secondary iron precipitates, including iron oxides and iron sulfides will act as a sink for arsenic, if any is remobilized.
Co-precipitation of arsenic as a trace component in oxyhydroxides or sulfides of iron or manganese	Dissolution of host oxyhydroxide due to decrease in pH or shift from oxidizing to reducing conditions; dissolution of host sulfide due to shift from reducing to oxidizing conditions.	
Adsorption to iron oxyhydroxides, iron sulfides, or other mineral surfaces	Desorption at high pH for oxyhydroxides and sulfides; complexation/stabilization in the presence of DOC. Reductive dissolution of iron hydroxides or oxidative dissolution of iron sulfides.	

* After EPA (2007)

Our laboratory testing showed that arsenic was retained in the iron + sulfide treated soil despite conditions that could, in theory, reverse the arsenic immobilization processes (Przepiora et al., 2008). The observed persistence of As-Fe reduced mineral phases in the iron + sulfide treated column under oxic conditions and extreme pH could be attributed to development of protective submicron iron oxide and oxyhydroxide coatings on As-bearing grain surfaces. Similar phenomenon has been observed in natural geologic systems where a primary or authigenic arsenopyrite is present on earth's surface (Craw et al., 2003). Based on this research, the As-Fe-S phases will be stable in water-saturated and moderately reducing systems, such as that created by the iron + sulfide based amendments.

METAFIX REAGENT: KEY BENEFITS

MetaFix Reagent represents a unique treatment approach for soil, sediment, industrial wastes, and groundwater contaminated with heavy metals. This customized reagent is designed to cost effectively address even the most challenging site conditions. The reagents are formulated blends of reducing agents, reactive minerals, mineral activators, catalysts, and pH modifiers. Following placement of the reagent into the treatment zone, a number of physical and chemical processes combine to create geochemical conditions under which common heavy metals are subjected to reduction, adsorption, precipitation, and conversion to stable sulfide and iron-sulfide precipitates. These heavy metal sulfide precipitates have greater stability than metal hydroxide precipitates, which are formed with traditional metals treatment approaches based on pH adjustment. Moreover, since the reagent utilizes multiple mechanisms, it allows for robust performance in challenging environments, with high metals concentrations, high concentrations of organic contaminants such as solvents, high salt content, or extreme pH levels. A custom MetaFix blend is developed based on a site's specific conditions through a low-cost treatability study to address soil and/or groundwater impacts.

The MetaFix approach offers a truly one of a kind, proprietary, customized solution for challenging metals sites.

- The proven ability to address multiple heavy metals including; Al, As, Cd, Cu, Cr, Hg, Ni, Pb, Se, V, and Zn.
- Superior Cr(VI) treatment with the formation of more stable mixed (Cr, Fe) hydroxides.
- The capability of treating comingled plumes of heavy metals and chlorinated solvents.
- Low overall treatment costs based on lower reagent dosing rates, as low as 0.1% to 4% (wt/wt), versus other metals treatment technologies.
- The treatment mechanism is not dependent on alkalinity for removal of metals, therefore not susceptible to rebound when the matrix pH returns to ambient levels.

APPLICATION METHODS

- Direct push injection
- Hydraulic and pneumatic fracturing
- Direct soil mixing
- Permeable Reactive Barriers

CONCLUSION

MetaFix is an innovation which represents an entirely new family of reagents for treatment of soil, sediment, industrial wastes, and groundwater contaminated with heavy metals. Their treatment mechanisms are based on iron, iron sulfides, and other iron-bearing minerals, and therefore result in heavy metal precipitates that include iron and/or sulfide. These iron/sulfide-bearing heavy metal precipitates generally have lower solubility, and greater stability, than precipitates that do not incorporate iron (i.e., heavy metal hydroxides). The new reagents are composed of mixtures of reducing agents (ZVI, iron sulfides), processed reactive minerals (iron oxides, iron oxyhydroxides), pH modifiers, silicates, and catalysts. This new approach is insensitive to toxicity, and performs well even in environments that have high metals concentrations, high concentrations of organic contaminants such as chlorinated solvents, high salt content, or pH levels (high or low) that would inhibit microbial carbon fermentation and sulfate reduction. Another unique advantage of these reagents is their ability to simultaneously treat heavy metals and chlorinated solvents. *In situ* reactive zones can be constructed to prevent migration of heavy metals into sediments or surface water.

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THE MIGRATION OF LNAPL IN SUBSURFACE AFFECTED BY SPILL VOLUME AND PRECIPITATION

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KEYWORDS
Image Analysis, LNAPL, LNAPL Migration, Precipitation, Subsurface Contamination

ABSTRACT

Groundwater contamination by *Light Non-Aqueous Phase Liquids* (LNAPLs) is known to increase environmental and health risks due to their toxicity and carcinogenic compounds such as BTEX and MTBE. Thisstudy isfocusedontheeffectsof spill volume and precipitation on one-dimensional migration of dieselinsubsurface. In this study, one-dimensionaltestswereconductedusinga 35 mm × 35 mm × 600mmcolumntosimulatedieselmigrationbehaviorin typical river sand and Toyourasandaffectedby diesel spilled volume and precipitationintensityconditions. In general, the high diesel spill volume caused deeper diesel migration at faster rate compared to the low diesel spill volume. When the infiltrated diesel reached a stable depth at capillary fringe zone, it no longer migrated deeper until this condition changes as soon as precipitation infiltrates the contaminated sand layer. Once precipitation started, diesel migrated downward into saturated zone. High intensity also led to high diesel migration rate, with an average of 2.1 mm/min, compared to low intensity case (0.3 mm/min). Thisshows that,althoughdieselis aLNAPL (ρ_{Diesel} = 0.865g/cm^3), precipitationcandisplace low-density contaminantsfurther down into the saturated zone,increasing the contamination degree of the groundwater.

INTRODUCTION

In today's industrial society, the utilization of non-aqueous phase liquid (NAPL) is very prevalent. From solvent to fuel oil, this organic hydrocarbon has served industrial evolution very well. In 2011, more than 86 million barrels per day were extracted worldwide (USEIA 2012), an extraction rate increase of 31% from 1991. Despite NAPL's good deeds for society, mismanagement of this chemical may have a negative impact on human health and the environment due to its toxicity.

With the huge amount of oil that needs to be managed, the oil industry faces the inevitable risks of accidental discharges into the ground and surface water either from tanker accidents (M. Ha et al. 2012), pipeline ruptures (Farias et al. 2008), or storage tank failures (Chang and Lin 2006). If the contamination discharge occurs underground, it will remain unnoticed until a nearby drinking water well becomes contaminated (Nadim et al. 2000). Groundwater contamination by Light Non-Aqueous Phase Liquids (LNAPLs), such as diesel, is known to increase environmental and health risks due to their toxicity and carcinogenic compounds such as benzene, toluene,ethylbenzene and xylene (BTEX) andmethyl tertiary-butyl ether (MTBE).

Groundwater fluctuation mainly occurs due to the recharge from rainfall and is also one of the contaminant migration agents (Flores et al. 2011). After the release of LNAPL into the subsurface, it can move through the pores within the soil due to gravitational and capillary forces. During this migration, the liquid leaves behind ganglia trapped and immobilized in the pores as non-drainable residual LNAPL (Wipfler and van der Zee 2001). High leaking volume may lead to downward migration and accumulation in the groundwater table. The groundwater fluctuation can cause vertical displacement and redistribution of LNAPL within the saturated and unsaturated zones.

Although it is well known that rainfall indirectly affects the vertical displacement of LNAPL through the fluctuating groundwater level, few researchers have focused on the direct effects of rainfall on LNAPL migration. The study of these effects is necessary in order to assess the LNAPL contamination plume when subjected to rainfall. When rainfall infiltrates unsaturated zones, the wetting front propagation will increase the soil saturation, changing the capillarity behavior and LNAPL migration behavior. The rainfall intensity can directly affect the infiltration behavior and the wetting front propagation velocity as well. Higher rainfall intensity may increase the wetting front propagation velocity and bring the mobile LNAPL deeper into the saturated layer, thus extending the groundwater contamination as it may migrate farther from the source.The objective of this study is to evaluate the effects of the spill volume and precipitation intensity on migration of diesel in the subsurface zone through a one-dimensional study using the Simplified Image Analysis Method (SIAM).

MATERIAL AND EXPERIMENTAL PROGRAM

A typical river sand and Toyoura sand was used as a porous medium in the one-dimensional study. Both sand can be classified as poor-graded sand(SP) according to the Unified Soil Classification System. The river sand specific gravity, G_s, is 2.60, equivalent grain size, $D_{50,}$ is 0.70 mm and void ratio, e, is 0.69. The Toyourasand particle density, G_s, is 2.63, equivalent grain size, $D_{50,}$ is 0.18 mm and void ratio, e, is 0.66. The LNAPL used in this study is diesel and is widely available in the world as it is a consumer fuel product, in general as a liquid fuel. Its density used in this study is0.865 g/cm^3, with viscosity of 7 mm^2/s, surface tension of 0.2675 N/m, and vapor pressure of 0.40 mm-Hg.

A 35 × 35 × 600 mm (sample: 35 x 35 x 500 mm) one-dimensional column with a front transparent acrylic wall was designed to study the LNAPL migration behavior in sand due to precipitation. A transparent acrylic wall was used as it provides a clear view of the liquid movement inside the sand column. SIAMwas used to obtain the soil saturation reading.The *Simplified Image Analysis Method* (SIAM)(Flores et al. 2011) is capable of measuring the saturation distribution values for water and NAPL in granular soils for a whole range of large domains instantaneously.Two consumer-grade digital cameras with two different bandpass filters (λ = 450 and 656 nm) were placed in front of the sand column to capture the images throughout the test. Fig. 1 shows the one-dimensional column set-up used in this study. Red Sudan III dye was used for LNAPL and Brilliant Blue FCF dye for waterto enhance visual observation and increase their light absorbance properties. Both dyes were used at concentrations of 1:10,000 by weight, without any noticeable change in the physical properties of water and LNAPL. The dyes are not absorbed or filtered by soil particles.

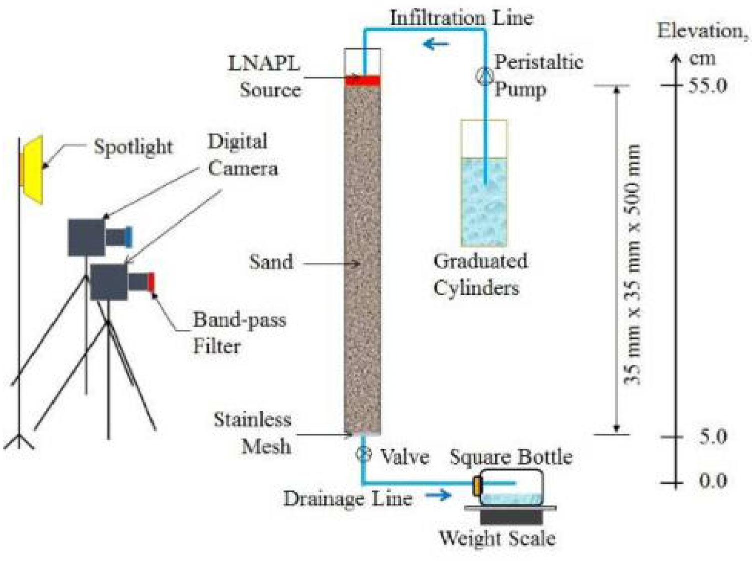

Fig. 1. One-dimensional column setup.

When LNAPL occupy the soil pores, it will alter the level of saturation of the soil. As the flow and migration of LNAPL is closely related to soil saturation, and its condition inside the soil pores, the variation in LNAPL spill volume was studied. In this study, the two values of LNAPL volume were used to represent a high and low spill volume condition. Four experiments were conducted using Toyoura sand during the study to cover the minimum and maximum range of LNAPL infiltration volume, V_D, and precipitation intensity, i. The low LNAPL infiltration volume condition used in this study was 25 mL (2.04 mL/cm^2), whereas the high was 50 mL (4.08 mL/cm^2). The low precipitation intensity used in this study was 6.5 mm/hr, whereas the high precipitation intensity was 63.2 mm/hr.The low diesel volume infiltration with high precipitation intensity condition will be called LH case hereafter. Low diesel volume infiltration with low precipitation intensity condition will be called LL case hereafter. High diesel volume infiltration with high precipitation intensity condition will be called HH case hereafter. Finally, high diesel volume infiltration with low precipitation intensity condition will be called HL case hereafter.

RESULTS AND DISCUSSION

At the start of the experiment, the fully saturated sand was allowed to drain by gravitational force. Due to the fact that sand has high permeability, the water drained relatively quickly, and the stable capillary fringe height could be seen in less than 6 hours. The high capillarity is due to the effect of fine grain size distribution in sand and can be seen clearly in all cases. The saturated capillary fringe could reach up to 260 mm of column height for river sand and up to 350 mm for Toyoura sand.

When the LNAPL spilled from the top of the column, it migrated downward due to the gravitational force and capillarity. Therefore, deeper LNAPL migration occurs in a larger spilled volume (Tab. 1), because it has sufficient pressure to overcome the capillary forces in order to advance into the finer pores filled with water.

Tab.1. LNAPL migration depth in river sand and Toyoura sand

LNAPL Spill Volume	Migration Depth (Toyoura Sand)	Migration Depth (River sand)
25 mL (2.04 mL/cm^2)	200 mm	
50 mL (4.08 mL/cm^2)	250 mm	300 mm
100 mL (8.16 mL/cm^2)		400 mm

While diesel infiltrated and migrated deeper, it had to overcome the capillary force; diesel ceases to migrate when it reaches equilibrium at interfacial tension. Although diesel density is lighter than water, due to the aforementioned mechanism, capillary depression occurred before equilibrium is reached. In our experiment, once the diesel infiltrated the sand and reached the top of the capillary fringe, the height of the capillary fringe was depressed for about 50 mm and 100 mm for 2.04 mL/cm^2 and 4.08 mL/cm^2 of spilled diesel, respectively (Fig. 2). A similar condition was also found by Chevalier et al. (1998), when an unleaded gasoline caused a 34 mm capillary depression of the water table. The result from our experiment is higher perhaps due to the higher diesel volume.

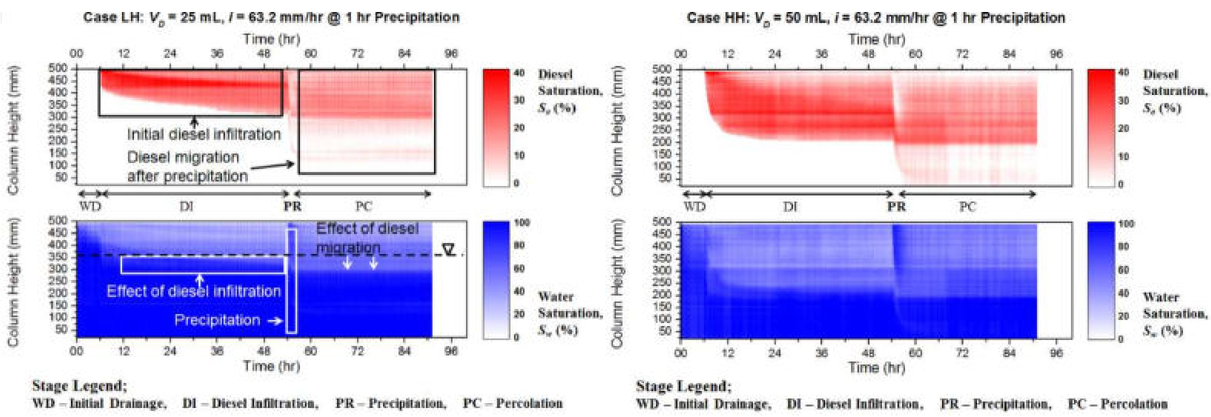

Fig. 2. Diesel and water saturation result for very heavy precipitation intensity cases.

In Fig. 2, it can be seen that the infiltration was faster for 50 mL (4.08 mL/cm^2) of diesel than for 25 mL (2.04 mL/cm^2) of diesel. This is mainly because the 4.08 mL/cm^2 had a higher volume and weight, which provided more pressure to push the diesel wetting front at a faster rate. It took about 6 hours for 4.08 mL/cm^2 to reach its stable depth compared to nearly 24 hours for 2.04 mL/cm^2 to reach its stable depth.

When the infiltrated diesel reached a stable depth, it no longer migrated deeper, because the two immiscible liquids, diesel and groundwater, had reached its interfacial tension equilibrium. This condition changes as soon as precipitation infiltrates the contaminated sand layer. The infiltrating water is subjected to gravitational force; as it tries to flow towards groundwater level, it will push down any diesel that it encounters. The mobilized diesel will be entrapped within the saturated capillary zone. Since diesel solubility is low, this condition causes a prolonged groundwater contamination risk of carcinogen and toxic compound release from diesel degradation.

The infiltrated water also caused the contamination plume to further depress into the capillary fringe around 50 mm downward in the saturated zone. In comparison with other LNAPL contamination study cases, a depression of capillary fringe up to 50 mm was also found for surfactant infiltrated gasoline (Chevalier et al. 1998) and 1-Butanol (Henry and Smith 2002). This means that, even without considering fluctuations of groundwater, the contamination plume can migrate deeper into the saturated capillary fringe zone and contaminate the groundwater.

In general, the higher the precipitation intensity, LNAPL will migrate more deeply due to precipitation. In all high precipitation intensity cases, LH (V_D = 25 mL) and HH (V_D = 50 mL), once precipitation started, a high volume of water supplied from high precipitation intensity infiltrated the sand and flowed downward due to gravitational force. This high amount of infiltrating water provided a high wetting front propagation force that pushed down any diesel (LNAPL) within its flow path. This mechanism helped diesel migrate easily into the saturated zone.

In the LH case, diesel migration occurred due to few non-wetting interconnecting bridges and high wetting front propagation velocity during precipitation. This could be the reason why high volumes of diesel mobilized and extended contamination deeper into the saturated capillary zone. The layers of high diesel saturation (25% to 30% of saturation) diminished and spread vertically with predominant diesel saturation below 20%.
High intensity led to a high diesel migration rate, with an average of 2.1 mm/min, compared to the low intensity case (0.3 mm/min). Consequently, a significant volume of diesel was pushed downward until it reached the bottom of the column and immobilized at the soil pores in the bottom layer inside the column. Since the intensity was high (i = 63.2 mm/hr), the water remaining in the column kept pushing the diesel until it reached a final stable condition, 80 mm deeper, 1 hour after the end of precipitation. Thus, diesel with a saturation value of 10% to 15% can migrate into the saturated zone, extend the contamination deeper, and increase the groundwater contamination risk.

CONCLUSIONS

This study simulated the rainfall effect on the one-dimensional contamination migration behavior of diesel (LNAPL) using different diesel volumes and precipitation intensity. From all experiments, it can be seen that the rate of diesel infiltration is much faster with a larger spilled volume. The capillary fringe depression occurs due to LNAPL spill; further depression occurs when subjected to precipitation. Both low and high intensity precipitations pushed the contamination plume deeper into the saturated capillary zone at least 25 to 150 mm. However, the more diesel contaminated the sand, the more it migrated deeper due to precipitation. When the precipitation intensity was low (i = 6.5 mm/hr), diesel reached a new stable condition during the precipitation stage. However, when intensity was high (i = 63.2 mm/hr), water remaining in the column kept pushing diesel until it reached a final stable condition, 80 mm deeper, 1 hour after the end of the precipitation. Furthermore, the high precipitation intensity caused more diesel to migrate downward into the saturated capillary zone, with diesel saturation around 10% to 15%. Therefore, if LNAPL contamination occurs, precipitation not only increases the contaminant mobility and makes it migrate further from the source, it also makes it goes deeper into the saturated zone.The experimental results show that although diesel is an LNAPL (ρ_{Diesel} = 0.865 g/cm^3), precipitation can displace low-density contaminants further down into the saturated zone, increasing the contamination degree of the groundwater.

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METHOD OF TREATING CONTAMINATED BROWNFIELDS USING GREEN TECHNOLOGIES

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KEYWORDS
Brownfields, contaminated soil, phytoremediation, landscape architecture, energetic plantations, citizen involvement

ABSTRACT

Industrialization has had a major effect on the environment. Many contaminants were released and accumulated into the soil causing major pollution. In order to rehabilitate the polluted areas, a method has been developed for greening brownfields using environmentally friendly technologies. This requires three phases and combines phytoremediation, energy recovery and landscape architecture for the reintegration of the area in the urban tissue. In this way, the plants used in the process receive triple valences: means of soil treatment, ornamental value and also energetic value. In order to apply the method, the case study of Cuprom was chosen, which is a former industrial area located in the city of Baia Mare, Romania. The site requires remedial action because of historical soil contamination with heavy metals, especially Cu, Pb and Zn. The potential of this area is very high because it has a very good location and infrastructure. The ecological restoration of the contaminated site is necessary in order to bring the soil close to its natural state and to reconvert it for the benefit of the citizens.

INTRODUCTION

National Environmental Protection Agency of Romania has compiled the national inventory in 2014 which recorded a number of 1183 potentially contaminated sites and 210 contaminated sites, a total number of 1393 affected sites.
The economic sectors that have significantly contributed to soil pollution are:
- Mining and metallurgical industry: 160 potentially contaminated sites;
- Petroleum industry: 861 potentially contaminated sites;
- Chemical industry: 37 potentially contaminated sites;
- Other activities (activities specific to the following industries: energy, electrical engineering and electronics, ceramics, glass, textile and leather, cement, wood, paper, machinery, food, activities specific to land transport, airports, activities specific to agriculture and stockbreeding, military activities, nuclear activities): 125 potentially contaminated sites (NEPA, 2015).

Industrialization in the Maramureş County from Romania had a major impact on the environment causing hot spots of soil pollution (Figure 1) due to the intense exploitation of land resources.

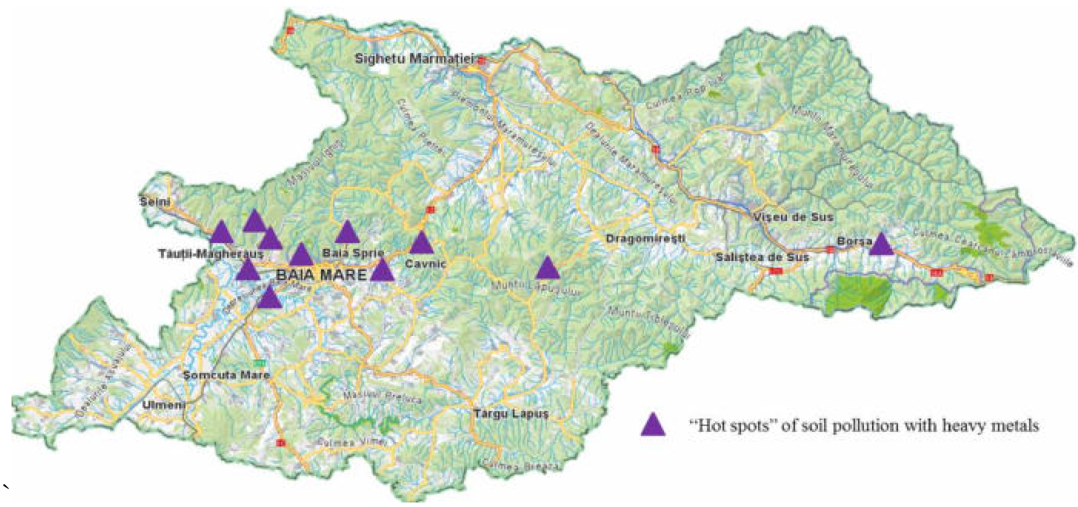

Fig. 1. Mining areas where soil pollution reaches the highest level in Maramureș County (Boroș et al., 2015).

REMEDIATION OF CONTAMINATED SITES USING GREEN METHODS

Heavy metal contaminated sites are very common in the case of former industrial sites. These areas should not be neglected, but converted for the benefit of local communities. To address the problem of soil pollution, one green remediation technology that can be applied is phytoremediation. Because of the large areas that industrial areas usually occupy, other remedial measures may become too expensive. If phytoremediation is combined with biomass production, the entire area can become a source of energy and a successful integration of a former industrial area. In addition, landscape architecture comes with more advantages using the design and redevelopment of the area to increase the value of the studied area. This will change public perception and improve the area economically, socially and aesthetically.
Because applying phytoremediation is a specific process for every site, standard procedures cannot be established, but general guidelines can be taken into consideration for each location and customized at each stage. The main objective of remediation projects of any contaminated site is to improve the current situation of each area in order to provide a safe and healthy environment for every citizen.
Former industrial area Cuprom is located in Baia Mare, a city with 100000 citizens in northwest of Romania. The area needs urgent measures of conversion because of its valuable location and because it is a central part of the city that needs to be integrated, not rejected.
Industrialization and urbanization in Baia Mare had negative effects on the environment due to pollution of important areas in the surroundings. Nowadays, the city must deal with the historical pollution and there is a lot of investment to be made to decontaminate the soil.
The Cuprom industrial area is polluted with heavy metals, mostly Cu, Pb, Cd and Zn (Damian et al., 2008). Rehabilitation of the entire area is necessary and further studies need to be undertaken regarding the possibilities of remediation. The current state of the case study can be seen in Figure 2.

Fig. 2. The actual state of former industrial site Cuprom, located in Baia Mare, Maramureș County of Romania.

The activities of the former Cuprom factory had led to soil contamination, copper having the biggest negative effect on the environment. Copper, due to its high concentrations in soil, may enter the food chain and it can affect human and animals' health. Because its concentration reaches the intervention threshold, urgent measures are needed to decontaminate the site and reintegrate it in the urban circuit of Baia Mare.

In the case of contaminated brownfields or active industrial sites, where the activities continue to release toxins in the surroundings, efforts of restoring the contaminated soil to a better state should be made in order to create new and stable ecosystems. Landscape architecture has a special purpose to transform the space and create stable ecosystems. Soil affected by human activities should be treated initially and continuously using phytoremediation. Plants that are chosen to clean the site, extract the contaminants from soil while they purify it. In this way, flora develops into a landscape of succession (Figure 3). The presence of any kind of vegetation indicates remediation success, while the lack of flora is a major indicator of the need of remedial measures. An abundance of new flora means that the new ecosystem can develop (http://www.draconaei.com/?p=1139).

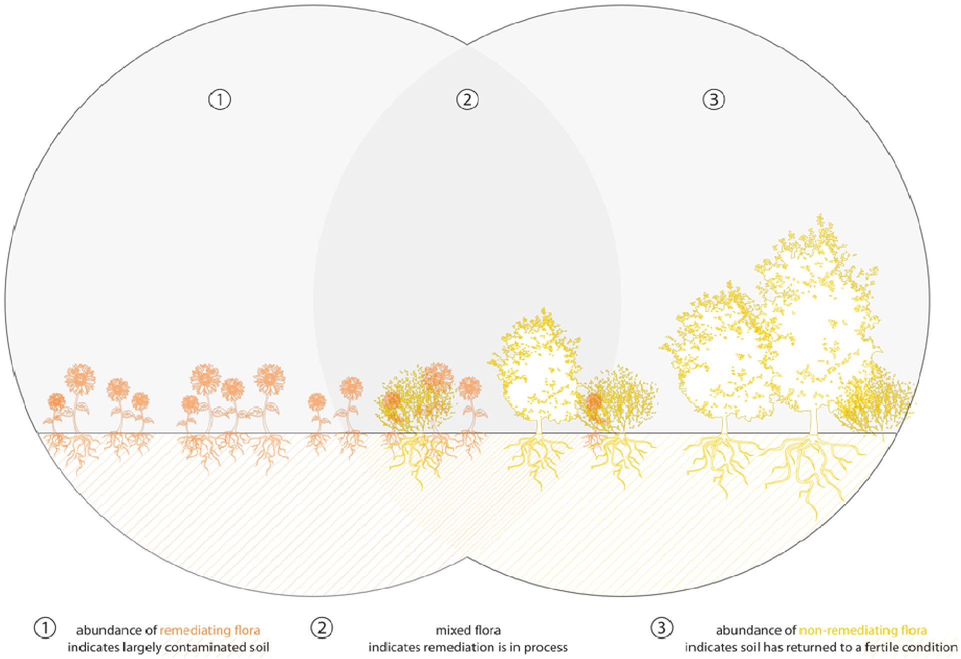

Fig. 3. Phases of restoring contaminated soil to fertile state (http://www.draconaei.com/?p=1139)

The benefits of creating new green spaces and using green technologies such as phytoremediation are:
- Creating or expanding ecosystem;
- The involvement and cooperation of the local community;
- Testing and implementing large-scale green remediation technologies;
- Flood control;
- Educational purposes;
- Improving the environment - improving soil, air and groundwater quality;
- Creating new public areas for recreation;
- Generating models for new projects of brownfields rehabilitation;
- Industrial heritage conservation;
- Economic improvement of the area;
- Identifying the sense of local community and social interaction;
- Improving the aesthetics of the area (Sousa, 2013).

Local communities must be involved in every step that is part of the redevelopment. The program's success can be associated with public participation and the future use of the area. In this way, conflicts and refusal of rehabilitation area because of noise, vibration due to the equipment used, the dust created during the process and other unpleasant activities are eliminated. The whole area is easily accepted by citizens and represents a reference area of local identity (Soesilo and Wilson, 1997; ITRC, 2006).

CONCLUSIONS

More or less, all countries are affected by human activities, urbanization and industrial development. During these processes, different types of pollutants are spread in soil and lead to environmental deterioration. Soil contamination is a major concern worldwide and requires solutions that are eco-friendly and also efficient.

Decontamination of brownfields is extremely important for the benefit of the environment and local communities. An innovative technique to clean these sites is phytoremediation. When large areas are required to be treated, phytoremediation is less expensive than the traditional techniques. Plants have already been used in various applications to help improve certain contaminated sites. A wide variety of sites can be decontaminated using phytoremediation. Numerous projects have been developed where it has been applied at large scale or in pilot projects.

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A NEW METHODOLOGY FOR THE REMEDIATION OF AN ACID TAR LAGOON IN MONS, BELGIUM

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KEYWORDS
acid tar, lagoon, remediation, neutralization, emission management, clean-up, hazardous waste, in-situ, soil mixing

ABSTRACT

The historical accumulated acid tar lagoon on former industrial site in Mons Belgium, was neutralized in the subsurface before excavation and transportation. The neutralized hazardous waste was then transported off the site to different licensed waste treatment facilities. For the neutralization of the acid tar an in-place mixing tool was used. The in-situ mixing technique is not a new technology but for the first time applied in an acid tar lagoon. Although other mixing tools have been used (Rompetrol, Vega Refinery, Romania), the neutralizing chemical was injected at depth by means of an automated dosing system. One of the evident advantages are the reduced emissions, mainly due to the limited handling of the acid tar prior to off-site transportation. Additionally, advantages in terms of heath & safety for the workers on-site, in terms of duration of the project and in terms of economics are achieved.

1. INTRODUCTION

Acid tar is a hazardous waste generated by refining processes, namely refining of benzole, refining of used lubricating oils or refining of petroleum by addition of sulphuric acid. Historically, acid tars were frequently dumped or stored on land in basins or lagoons in an uncontrolled manner causing contamination of land, surface water and groundwater.

The composition of acid tar is complex and very variable. It is function of the refining process, the process conditions and the quantity of sulphuric acid used. Acid tars composition is a mixture of sulphuric acid, hydrocarbons, water and ash. Heavy metals are also potentially present, such as mercury and arsenic. Gases of hydrogen sulphide, sulphur dioxide and volatile organic compounds vapours (BTEX) are released, especially when the waste is handled.

2. THE ACID TAR LAGOON IN MONS

2.1. History of the site

In 1884, cokes ovens and a facility for the recovery of coke residue were in operation on site. By the late 1920s, the activities expanded with a benzole refining and a tar distillation plant. The coke ovens were decommissioned in 1928. The facility for the recovery of coke residue received residues from neighbouring coke factories and stayed in operation until 1960. In 1985 all the facilities were decommissioned. During this period, the residual tars from the benzole refining and wastes from other activities were dumped on land and covered with soil. Approximately 1 hectare was impacted and 20.000 tons of pure tar were found.

Because of the size of the whole industrial complex, the site needed a phased approach. The rehabilitation and remediation works started in 2009 and only in 2015 the acid tar waste dump was under remediation. SPAQuE (public company of the Walloon Region) appointed SUEZ for the phases 3 to 6. The works in phase 6 included the remediation of the acid tar lagoon, while the works in phases 3 to 5 covered the remediation of some hot spots and highly contaminated soils.

2.2. Characteristics of the acid tar

The acid tar present on site arises from the refining of benzole by addition of sulphuric acid, resulting in tar with a very low pH, with considerable impacts from sulphur and VOCs, in particular benzene and toluene.

Fig. 1. Acid tar rising through covering material and spreading laterally across the surface.

The top layer of the acid tar is dusty and crusty , in total a couple of inches thick. Figure 1 shows the top layer of the acid tar. The subsurface acid tar surfaces in a vulcano like manner through the covering material and spreads laterally across the surface. The tar becomes relatively solid, but still viscous below the top layer and the properties of the tar becomes more liquid and granular at depth.

Due to the addition of sulphuric acid, the tars are severely acidic and contain a high sulphur content. The pH of the tars is very variable. Locally pH values below 1 are encountered, however pH values ranging from 1 to 3 are more commonly measured. The sulphur content of the acid tar reaches locally 15%, but values ranging from 2% to 7% are more commonly measured. The tars originate from the refining of benzole and as a result contain high concentrations in volatile organic compounds. Benzene concentrations are reaching 65.000ppm and the total BTEX concentration 100.000ppm. Emissions of hydrogen sulphide and sulphur dioxide originate from the acid tar, especially when the waste is handled. Table 1 summarizes the composition of acid tar and highlights the heterogeneity of the material.

Tab. 1. Composition of the acid tar, minimum and maximum values of the main components

Parameter	Unit	Min – Max values
pH		0 – 4
Sulphur	%	2 – 15
Benzene	ppm	4.000 - 65.000
BTEX	ppm	6.000 - 100.000
TPH C10 - C40	ppm	10.000 - 32.000
PAH-16	ppm	200 - 2.700
As	ppm	250 - 1.200
Hg	ppm	1 - 30

3. THE SITE REMEDIATION WORKS

3.1. The remediation plan

The remediation plan defined by SPAQUE consists mainly of:

- Removal of the pollution source or the acid tar until reaching the soil layer.
- Verifying that the remediation objectives are met by sampling and analyzing the excavation at the base of excavation and sidewalls. Further excavation may be required to comply with the remediation objectives set by SPAQUE.
- Neutralization of the acid tar on-site before transport to approved waste treatment facilities.
- Emission management, control and mitigation.
- Backfilling using clean soils.

3.2. Preliminary works

Prior to commencement of the remediation works, SUEZ performed a detailed study of the acid tar lagoon. The study consisted of

- Mapping of the contaminated area: a thorough characterization of the area is performed by collecting and analyzing tar and soil samples.
- Laboratory tests to determine the most suitable neutralization additive and the required quantity to achieve the objective of pH, value set between 4 – 13.
- Air quality measurements during trial pit excavations.

Mapping of the contaminated area consisted of borehole logging and sample collection every 10m square grid. Approximately 50 drillings are performed and 100 samples collected. With the borehole logging, the thickness and extent of the acid tar is assessed. Figure 2 shows the geological sections of the area.
Based on the laboratory tests and for each 10m square grid, a quantity of neutralization product is evaluated. As shown in table 1, the pH of the tar is very variable and the quantities added to reach the objective vary from approximately 2 to 15% (by weight).

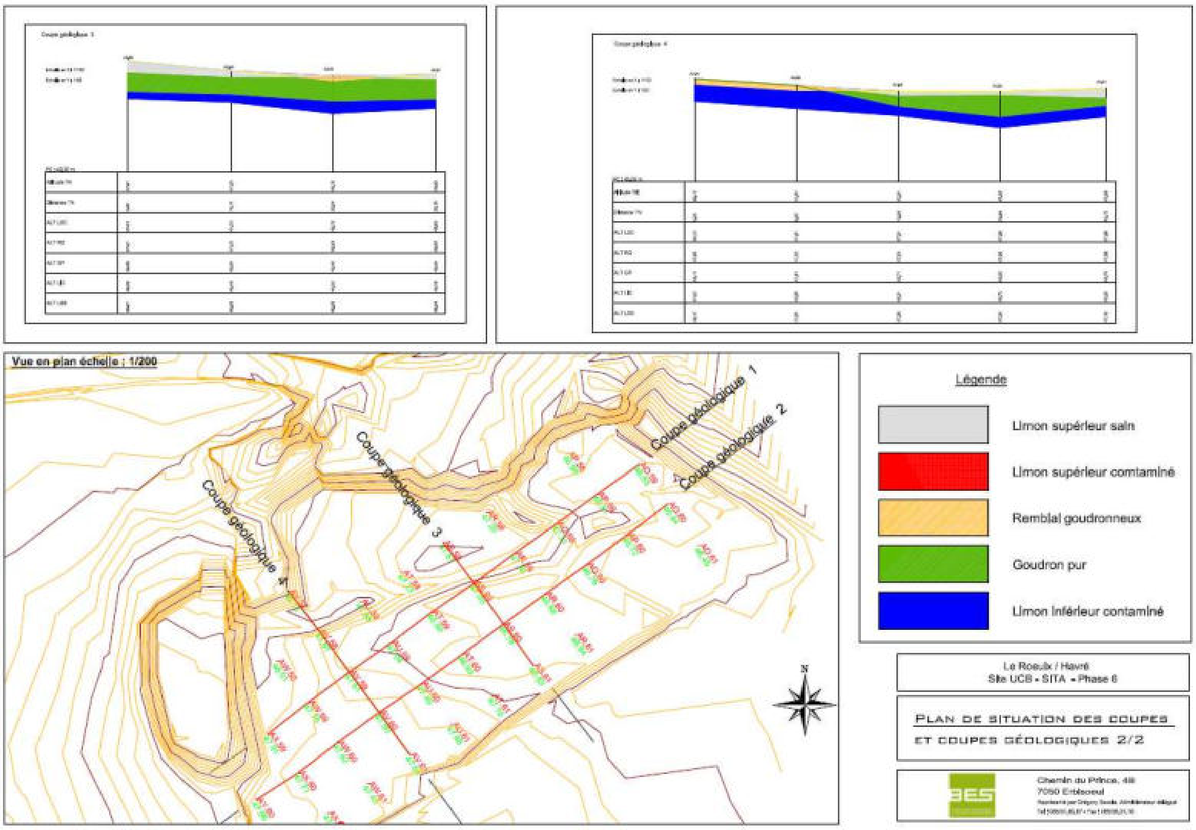

Fig. 2. Map with geological sections of the acid tar area. In green, the acid tar layer. In blue, the silt layer.

Air quality measurements are also performed during trial pit excavations to evaluate the measures necessary to ensure health and safety for the workers and residents during the remediation works. One of the parameter measured is the total volatile organic compounds (TVOC). The results for the TVOC are shown in figure 3. Peaks of 800ppm and 330ppm are measured at respectively 5m and 20m from the trial pit. As the threshold limit value (TLV) for benzene is 1ppm or 3,25 mg/m³, supplied-air breathing apparatus is required for personnel working in the acid tar area. The TLV is the concentration in air to which it is believed that most workers can be exposed daily without an adverse effect.

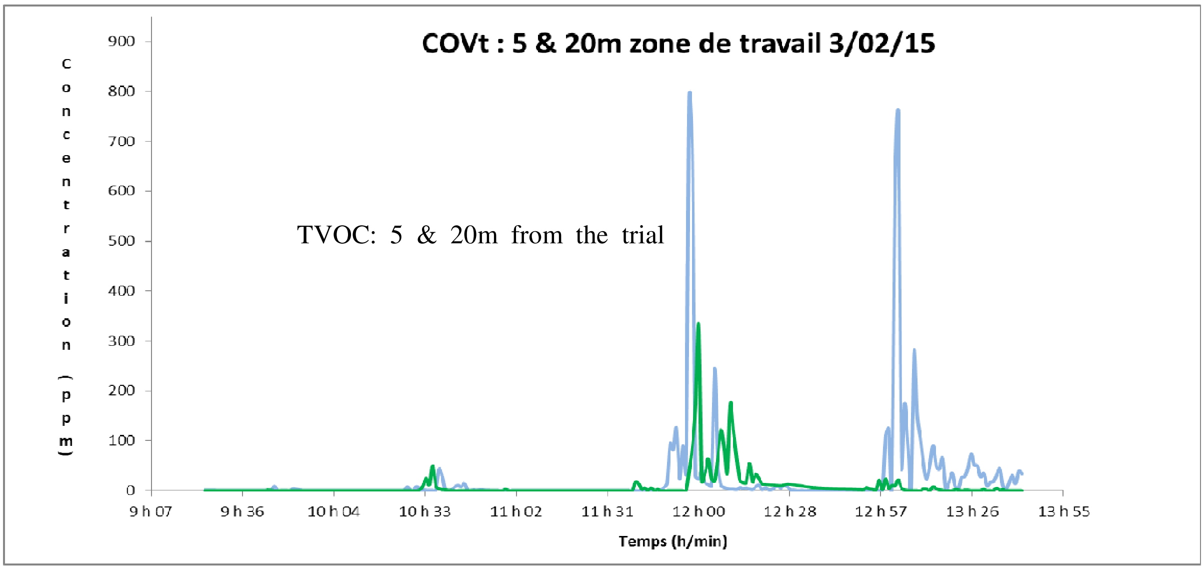

Fig. 3. Concentration of TVOC in the air (ppm) in function of time and distance from the trial pit. In blue, 5m distance from the trial pit. In green, 20m distance from the trial pit.

3.3. Neutralization methodology and acid tar treatment

The acid tar is neutralized on-site before being transported to approved waste treatment facilities for further treatment. Neutralization is performed by mixing the neutralizing additive with the tar using a hydraulic mixing tool mounted onto an excavator. A mobile feeder is connected to the excavator and feeds the additive by compressed air in the middle of the mixing tool. The feeder is equipped with a weighing system allowing to control the quantity added into the acid tar. Figure 4 shows the equipment the mobile feeder and mixing tool.

Fig. 4. Equipment used to neutralize the acid tar. On the left, the mobile feeder. On the right, the excavator equipped with the mixer.

After reaching the pH target value, the acid tar is removed and transported to approved waste treatment facilities. The most cost-effective treatment method is selected. The choice of treatment depends on several parameters, such as calorific value, sulphur content, concentrations in mercury, arsenic and benzene. The treatment techniques used for the acid tar are:

- Co-incineration in cement kilns;
- Incineration with energy recovery;
- Thermal treatment by pyrolysis;
- Thermal desorption.

3.4. Emission management and health and safety measures

Ambient air quality monitoring is performed during the remediation works and includes near-source and perimeter monitoring stations. The near-source monitoring stations are measuring TVOC, benzene, SO2, H2S in the air during the working hours. If near-source ambient air quality limits are exceeded, actions are triggered to reduce emissions before reaching the surroundings. The perimeter monitoring stations are located close to the site boundary and are measuring 24h/24 and 7d/7, TVOC, benzene, toluene, SO2 and PM10. PM10 is the atmospheric particulate matter with a diameter of 10µm or less. In addition, the wind direction and speed is continuously measured.

Various measures are taken to mitigate emissions from the neighbouring surrounding environment. When air quality limits are reaching emission reduction measures are triggered, such as:

- Reducing the size of the in-situ neutralization or excavation area.
- Covering of the acid tar with compost or foam.
- Use of a water spraying system with odour control agent to reduce odor nuisances.
- Use of an air ventilation system to blow air away from the receptor.
- Stop remediation when the wind is unfavourable (or in the direction of the closest receptor).

For health and safety concerns, the hazardous properties of the acid tar require the use of chemical and acid resistant gloves, boots, overalls and respiratory protection for all personnel working or entering the area. The respiratory protection is a self-contained breathing apparatus with an independent air supply. Figure 5 shows the full set of personnel protection equipment.

Fig. 5. Left, full set of PPE with self-contained breathing apparatus. Right, compressed air bottles connected to the cabin of an excavator.

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GENTLE REMEDIATION OPTIONES (GROS) ON PB/ZN CONTAMINATED SITES IN AUSTRIA – EXAMPLES FROM THE GREENLAND-PROJECT

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KEYWORDS
Mining and smelting, in-situ remediation, phyto-technology, gentle remediation options

ABSTRACT

Mining and processing activities affecting many sites worldwide negatively. The huge amounts of moved and treated materials have led to considerable flows of wastes and emissions. Alongside the many advantages of processed ores to our society, adverse effects in nature and risks for the environment and human health are observed.

The GREENLAND-project brought together “best practice” examples of several field applied gentle remediation techniques (EUFP7-project “Gentle remediation of trace element-contaminated land – GREENLAND; www.greenland-project.eu) with 17 partners from 11 countries and has been launched in 2011 until the end of 2014. Gentle remediation options (GRO) comprise environmentally friendly technologies that have little or no negative impact on the soil. The main technologies are phytoextraction, in situ immobilization and assisted phytostabilization.

Three stages of impact of Pb/Zn-ore-treatment on the environment are discussed here: (1) On sites where the ores are mined impacts are the result of crushing, grinding, concentrating activities, and where additionally parts of the installations remain after abandoning the mine, as well as by the massive amounts of remaining deposits or wastes (mine tailings). (2) On sites where smelting and processing takes place, depending on the process (Welz, Doerschel) different waste materials are deposited. The Welz process waste generally contains less Cd and Pb than the Doerschel process waste which additionally shows higher water- extractable metals.(3) On sites close to the emitting source metal contamination can be found in areas for housing, gardening, and agricultural use. Emissions consist mainly from oxides and sulfides (Zn, Cd), sulfates (Zn, Pb, and Cd), chlorides (Pb) and carbonates (Cd).

All these wastes and emissions pose potential risks of dispersion of pollutants into the food chain due to erosion (wind, water), leaching and the transfer into feeding stuff and food crops. In-situ treatments have the potential for improving the situation on site and will be shown by means of field experiments in Spain, Poland and Austria.

(1) In the abandoned Pb/Zn-mine in Rubiais in Lugo (ES) plant growth at some spots across the tailings is almost impossible due to high contamination and further adverse chemical, physical and biological conditions, despite a precipitation of 2000 mm/a. Despite these conditions a few plant species (Cytisus, Betula and Salix) were found to tolerate these conditions and some were selected for further application in field trails established at this site. Cytisus species are perennial, leguminous plants and widely distributed, making them interesting candidates for re-vegetation and phytostabilisation of highly metal-contaminated soils. Salix species show a high potential for revegetation and mechanical stabilisation of the easily erodible soil, and some species are able to accumulate relatively high concentrations of Cd/Zn in aboveground parts.

Fig. 1. View from the top on mine Rubiais in Lugo in Spain (field experiment in the center).

(2) On smelting waste deposits in Piekary in Silesia (PL) municipal biosolid mixtures were applied generating a milieu where plant cultivation is possible (precipitation 800 mm/a) to reduce the erosion and leaching of contaminants. Welz and Doerschel process wastes were treated in different ways which is reflected in the different application rates of amendments.

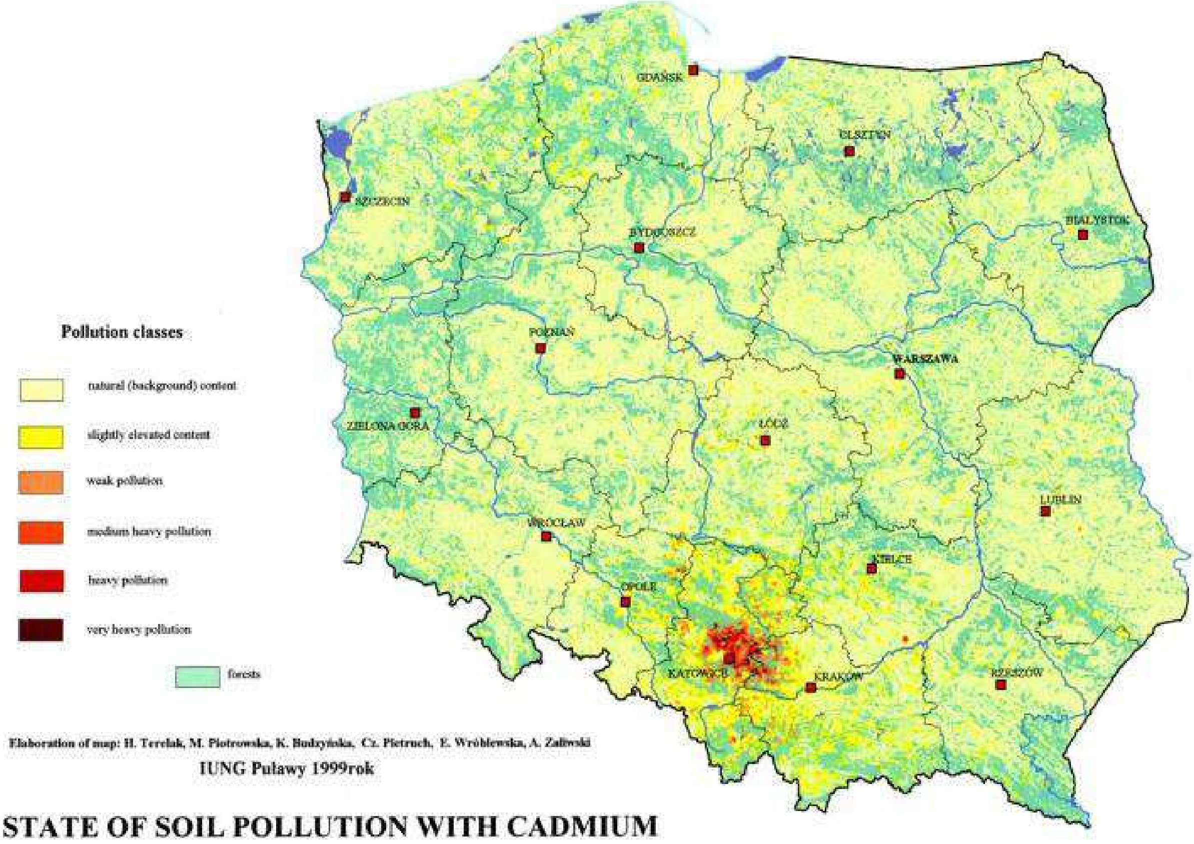

Fig. 2. Cadmium contamination in the Katowitze region in Poland.

(3) On agriculturally used land in the vicinity of the Pb/Zn smelter (BBU) in Carinthia, soil amendments were applied and shown to effectively reduce the contaminant uptake in feeding crops. Additionally heavy metal excluding cultivars were selected which further reduced the unwanted uptake. These contaminated sites pose, in addition to the recent acute risks, also a long-term risk which should be reduced by appropriate in situ measures. The shown techniques and methods can contribute to a reduction of these risks and to improvements at these sites for the environment and human health.

Fig. 3. Recent emisions in the area of the former smelter site in Austria (85 m high stack is not emitting anymore) (Foto Klaus Platzer, 2004).

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CHELANT – BASED SOIL WASHING FOR METAL CONTAMINATED SOILS: PILOT/DEMONSTRATIONAL REMEDIATION PLANT

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KEYWORDS
EDTA, soil washing; pilot plant, demonstration phase, toxic metals removal, soil functioning

ABSTRACT

The potential of aminopolycarboxylic chelants for soil Pb removal and bioaccessibility stripping is well known. The most frequently used is ethylenediamine tetraacetate (EDTA) because of low toxicity, high efficiency for toxic metal removal and relatively low price. Soil washing (extraction, leaching, flushing) where EDTA and toxic metals forms water-soluble complexes (chelates) and used washing solution is separated from the solid phase is straightforward operation. However, chelates which partly remained in washed soil are compounds with high degree of stability and must be further removed by extensive soil rinsing. What makes remediation difficult is treatment of large volumes of generated effluents, preferably to recycle both EDTA and process waters. We are presenting the development of a new, effective and emission-free soil washing technology and our research on the treated soils' overall health, functioning and potential use after remediation. Contruction of pilot plant with capacity of 6t/day is in the process of construction in Slovenia and is co-financef from LIFE+ Programme.

Calcareous soil from Meza Valley, Slovenia and acidic soils from Arnoldstein, Austria and Pribram, Czech Republic (with 1028, 862 and 926 mg Pb kg-1, respectively) were washed with 60-100 mmol kg-1 EDTA in series of 30 batches (50 kg batch-1). Technology features novel reaction of alkaline substitution, precipitation and adsorption of toxic metals on polysaccharides and chelant acidic precipitation for in average 83% EDTA and complete process waters recycle (no wastewater was generated). The pH gradient was imposed by Ca(OH)2 and H2SO4; the reagents' excess was removed with remediated soil as an inert CaSO4, thus to prevent saltification of recycled process waters (Figure 1). Remediation removed 60, 78 and 71% of Pb from Meza, Arnoldstein and Pribram soils, respectively, and reduced Pb bioaccessibility into simulated human gastro-intestinal phase (assessed using UBM) by 5.0-, 7.7- and 8.1-times, respectively. Residual emissions (EDTA, toxic metals) were prevented by soil ageing and deposition of remediated soil on reactive permeable barrier. The solid wastes from process amounted to 10.8 kg t-1 of soil and the material /energy cost of remediation up to 20.6 € t-1.

Sustainable soil use after remediation was investigated for Meza soils. The effect of remediation on soil physical and chemical properties and soil functions were minor and reparable (Jelusic et al., 2013; Zupanc et al., 2015). Revitalization measures for restoration of soil fertility and plant fitness included fertilization with Mn and hydrogel amendment to improve soil water holding capacity (Jelusic et al., 2014b). Sequential extractions did not reveal long-term reversal of reduced bioaccessibility of toxic metals (Jelusic et al., 2014a). Safe vegetable production has been demonstrated after soil washing of originally medium contaminated soil (Jelusic et al., 2014c). Use of remediated soil as a substrate for ornamental plants and grasses was studied and proposed for originally highly contaminated soils, unsuitable for food production (Jelusic et al., 2015). Significant spatial reduction of toxic metals (Pb, Zn and Cd) contamination and reduction of Pb blood levels in children before and after soil remediation and have been modeled and predicted for Meza Valley (Finzgar et al., 2014; Jez et al., 2015).

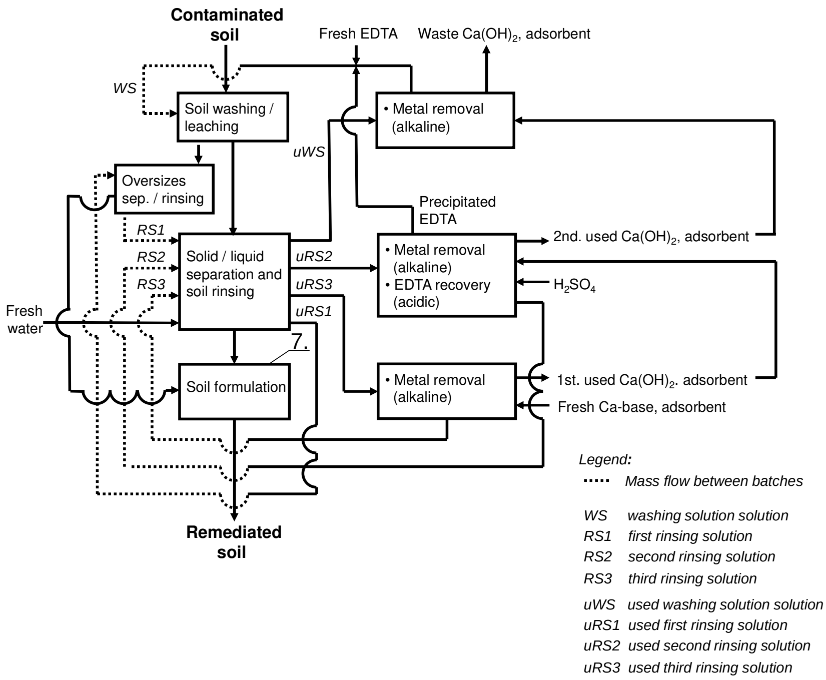

Fig. 1. Flowchart of the novel soil washing technology.

Construction of a demonstration plant with proposed soil washing technology began in 2015. The plant is situated in Meza Valley, Slovenia. The plant will have a capacity of 6 tons of contaminated soil per day. The purpose of the plant is demonstration of the proposed soil washing technology. The first batches are expected to be remediated till the end of the 2016. The construction and first year of operation is co-financed by the LIFE + program, project ReSoil LIFE12 ENV/SI/000969 (http://liferesoil.envit.si). Slovenian legislation requires building permit and Environmental permit for waste processing for the construction of a demonstration facility. For proposed capacity of soil remediation obtaining of the Environmental protection consent is not necessary, although it is necessary to submit an application.

Fig. 2. Demonstration plant for soil washing technology.

Reactions and processes used in novel technology were able to absorb and neutralize fluctuations of measured parameters without operator intervention throughout the series of remediation batches, demonstrating the adjustability and resilience of the novel technology for different soils and chelant inputs. Remediated soil retained quality and provided ecosystem services, including safe food production. A demonstrational remediation plant using scale-up of the novel technology is under construction in the Meza Valley, Slovenia.

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INDUSTRIAL SOLUTION FOR HEAVY CONTAMINATED SLUDGES WASTE WATER TREATMENT SLUDGE AL-MADINAH SAUDI ARABIAN KINGDOM

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SAVATERRA Oy, Finland

KEYWORDS
Organic sludge, microbiological risk, microbiological contamination, fertilizers, pathogenic contamination

ABSTRACT
The samples obtained from KSA were as follows **i)** one was raw fresh sludge from the waste water treatment plant and **ii)** one from dried sludge piles in the waste water treatment plant site.Sludge free laying in Al Madinah Water treatment plant in amount of millions tons is microbiological very dangerous – its hazardous pathogenic compounds are very active and dangerous for people. Sunny drying of sludge is not effective for pathogens killing, sample analyzes exactly prove huge existence of live dangerous pathogens out of safe limits in the case of longer rains the pathogens will transport by water into eating chain, it is only limited time for solving this problem and managing this real risk, only volume of rainwater is decisive to direct jeopardy human healthy.
Both samples had *E.coli* more than EU allows in the organic fertilizers meant to be used e.g. in agriculture. Raw had 13000 cfu/g (colony forming units) per gram of material. The dried sludge (sun dried) had also over the limits 6000 cfu/g. The allowed amount in EU is max. 1000cfu/g. *Salmonella* was also detected in the dried sludge (detected in 25g sample). Both samples contained *Clostridium perfringers* more than >100 000 cfu/g.
Based on these "normal" analysis both material have high degree of microbial contamination risk for humans, animals and plants. Especially interesting was the fact that sun drying DID NOT KILL pathogens! Therefore the dried sludge remained possible health hazard.

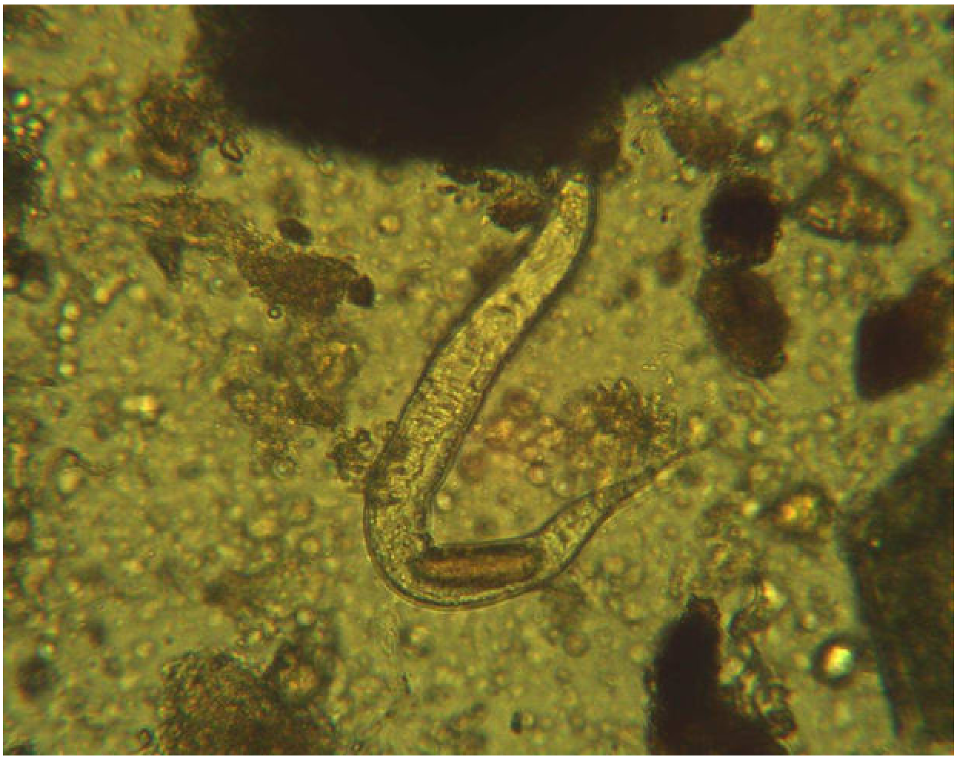

Fig. 1. Bacteria, worm eggs, fungus spores, worm, paramecium

Process of hygienization microbiological risky sludge by SVATERRA Oy company was tested. The new sludge is mixed with old sludge and if needed green waste. The mixing ratios will be determined before the trial in Al Madinah, Kingdom of Saudi Arabia. The product after the treatment fulfils European directives on the organic fertilizers (EU 71/2006). -The product can be used after treatment for fertilizer, agriculture or gardening purposes. The estimated area of the treatment plant is 60*40m.

SAVATERRA Oy prepared product fulfils the microbiological and chemical quality of the European directive on the organic fertilizers (EU 71/2006, HE 71/2006).

PRODUCT CERTIFICATE:

Name of product OSIF - Organic soil improving fertilizer

Trade name Organic soil improving fertilizer

Raw materials Waste water treatment facility sludge

Production process The sludge are hygienized as the first step. All viruses, bacterial and all other harmful contaminants are killed. Nutrients remain intact. The product is then agitated and inspected and approved by authorities for selling.

Use of the product The product can be applied for agriculture purposes, and to replace artificial fertilizers.
The product can be used for green building purposes and prevent erosion.

How to use? If the soil pH is under 5.5, calcium should be applied for the soil to pH levels suitable for plants. The organic fertilizer is then mixed into soil to 20cm depth. The nutrient level of soil is inspected before applying the use of organic fertilizer to have calculate proper amount of use per hectare of soil. Usually amount of 13-20 metric cubics of the fertilizer per hectare can be used.
Book keeping of the use is recommended to have.

	Analysis method		Value	
pH	SFS-EN 13037	6,5		
Conductivity	SFS-EN 13038	120	mS/m	
Total nitrogen (N)	SFS-EN 13654-2		3,9	kg/m3
			22000	mg/kg
Water soluble nitrogen (N)	SFS-EN 13652	0,50	kg/m3	
			3000	mg/kg
Total phosphorus (P)	SFS-EN 13650	3,3	kg/m3	
			20000	mg/kg
Water soluble phosphorus (P)	SFS-EN 13652	0,030	kg/m3	
			180	mg /kg
Total potassium (K)	SFS-EN 13650	0,230	kg/m3	
			1400	mg/kg
Moisture	SFS-EN 13040	70	%	
Density	SFS-EN 13040	550	kg/m3	
Amount of organic material	SFS-EN 13039	60 % dry mater		
Coarseness	Product is not sieved			
Weed seeds	Product might contain wild spreading seeds			

Amount of metals (average)	Max. concentration		Units mg/kg of dry material
As	SFS-EN 13650	5	
Hg	SFS-EN 13650	0,5	
Cd	SFS-EN 13650	0,7	
Cr	SFS-EN 13650	40	
Cu	SFS-EN 13650	350	
Pb	SFS-EN 13650	30	
Ni	SFS-EN 13650	20	
Zn	SFS-EN 13650	600	

Origin of the Product Kingdom of Saudi Arabia

Technology producer company Savaterra Oy has a full scale reference in Helsinki Water's sludge treatment in Sipoo Metsäpirtti sludge treatment area for 100 000t per year since 2008. The sludge is being treated by Savaterra according to (EU 71/2006, HE 71/2006) demands on the organic fertilizer for soil improving material.

List of wastewater sludge treatment:

1) Helsinki Water Company since 2008 and has been treating altogether so far <1 000 000t of the material.
2) City of Vaasa, Finland sludge originating mixed biowaste and sludge from anaerobic digesting 10 000t according to EU 71/2006 legislation.
3) City of Storfors, Sweden 10 000t sludge from aerobic waste water treatment plant according to EU 71/2006 legislation.
4) City of Käppälä, Sweden 10 000t of the sludge originating from aerobic waste water sludge treatment facility according to EU 71/2006 legislation.

The process for the sludge hygienisation has been developed and patented by Savaterra and the plant has been manufactured by Kalottikone Oy which is Savaterra's sister company. Kalottikone has a long history as specialised machinery house.


METSÄPIRTIN PUUTARHAMULTA
Tuoteseloste

Tyyppinimi	Kompostimulta
Kauppanimi	Metsäpirtin Puutarhamulta
Raaka-aineet ja valmistus	
Käyttötarkoitus	
Käyttöohjeet	

	Analyysimenetelmä	Tavoitearvo
pH	SFS-EN 13037	6,1
Johtokyky	SFS-EN 13038	70 mS/m
Vesiliukoinen typpi (N)	SFS-EN 13652	160 mg/l 200 mg/kg ka
Liukoinen fosfori (P)	SFS-EN 13651	60 mg/l 90 mg/kg ka
Liukoinen kalium (K)	SFS-EN 13651	750 mg/l 850 mg/kg ka
Kosteus	SFS-EN 13040	50 %
Tilavuuspaino	Myyntikosteudessa	900 g/litra
Orgaaninen aines	SFS-EN 13039	19 % kuiva-ainesta (ka)
Karkeusaste		alle 20 mm
Rikkakasvin-siemenet		

Haitalliset metallit	Enimmäispitoisuudet	Yksikkö mg/kg kuiva-ainetta (ka)
arseeni	SFS-EN 13650	5
elohopea	SFS-EN 13650	0,2
kadmium	SFS-EN 13650	0,2
kromi	SFS-EN 13650	20
kupari	SFS-EN 13650	70
lyijy	SFS-EN 13650	12
nikkeli	SFS-EN 13650	12
sinkki	SFS-EN 13650	150

Alkuperä- ja valmistusmaa: Suomi

Valmistaja ja myyjä: Helsingin Vesi, PL 1100 (Ilmalankuja 2 A), 00099 HELSINGIN KAUPUNKI

HELSINGIN VESI

Metsäpirtti trädgårdsmylla

Metsäpirtti TRÄDGÅRDSMYLLA

Näringsämnen tillbaka till naturen

Fig. 2. EU - Finland Product Certificate.

SAVATERRA Oy successfully patented this process in 2008.

The product fulfils the microbiological and chemical quality of the European directive on the organic fertilizers (EU 71/2006, HE 71/2006). The growth yield with product compared to normal growth peat is very good.

The objective in hygienization is to provide a proper nutrient balance and environment for the reproduction of aerobic thermophilic bacteria. Factors such as temperature, moisture content, structure, and proper aeration are critical to efficient hygienization. Operating temperatures of 80 to 90 degrees Celsius are desirable during the aerobic hygienization process. These temperatures kill fly larvae, pathogens, and weed seeds.

Fig. 3. Hygienization line photo.

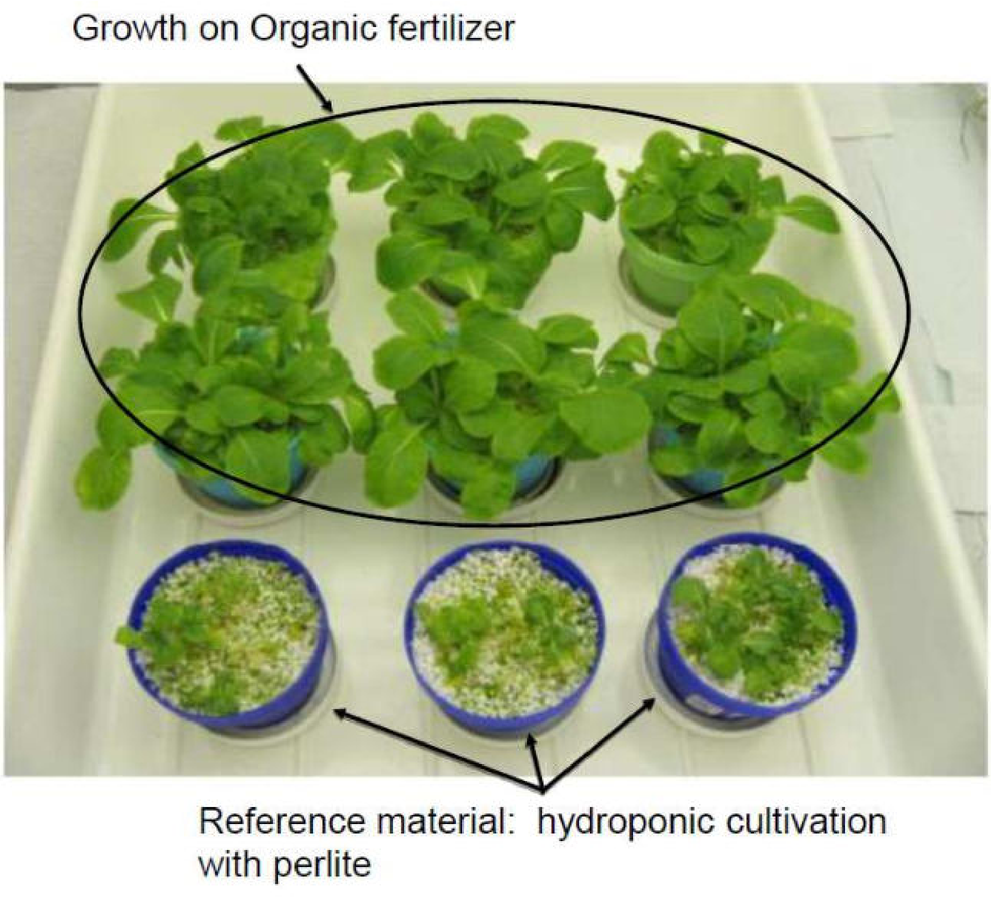

Fig. 4. The growth yield with product compared to normal growth peat.

TRAIN TECHNOLOGY - AN IRON-BASED MICROBIAL REMEDIATION AN EXAMPLE OF CONBINED TREATMENT APPROACH

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KEYWORDS
Iron reducing bacteria, chlorinated hydrocarbons, treatment train approach

ABSTRACT

Iron reducing bacteria are capable of using iron (III) oxides as their terminal electron acceptor. They belong to the main natural drivers of iron cycle in the environment. During iron (III) respiration, ferrous ions are released. This form of iron does not rank among the most stable and it is very probable that ferrous ions will react with other compounds to achieve the origin oxidation number. Among mentioned compound, many anthropogenic compounds may be classified, for instance chlorinated ethenes or some toxic metals. Moreover the same compounds may serve as the source of reducing equivalent for iron reducing bacteria. The technology TRAIN has been designed for cost effective remediation purposes. In this contribution, a case study describing the full application in operation environment will be presented in order to emphasize original remediation strategy based on synergetic effect integrated into the technically easy applicable solution.

THEORETICAL BACKGROUND

Iron reducing bacteria (IRB) represent key microbiological drivers in different metal and carbon cycling (under anaerobic conditions). They carry out such mass transformations from biogeochemical view that can have a significant potential for both intrinsic bioremediation so for engineered remediation treatment. Many strains of IRB prefer close contact with iron materials (both natural - iron bearing minerals, so artificial - rust on oxidized iron surface for dissimilatory releasing of ferrous ions resulting in microbial respiration - growth). For their sustainable existence, these bacteria must migrate between iron particles. Thus, a key question is how such organisms can sustain growth under these conditions. Microscopic results at the absorption edges indicate that nanoparticle aggregates contain a variable mixture of Fe(II)–Fe(III), and are generally enriched in Fe(III). *Geobacter bemidjiensis* cultivated anaerobically in the laboratory on acetate and hydrous ferric oxyhydroxides also accumulated iron particle aggregates. In samples collected from field areas, IRB with a wide variety of morphologies were associated with small aggregates, indicating that cell surface Fe(III) accumulation may be a general mechanism by which it can grow while in planktonic suspension (Luef, 2013).

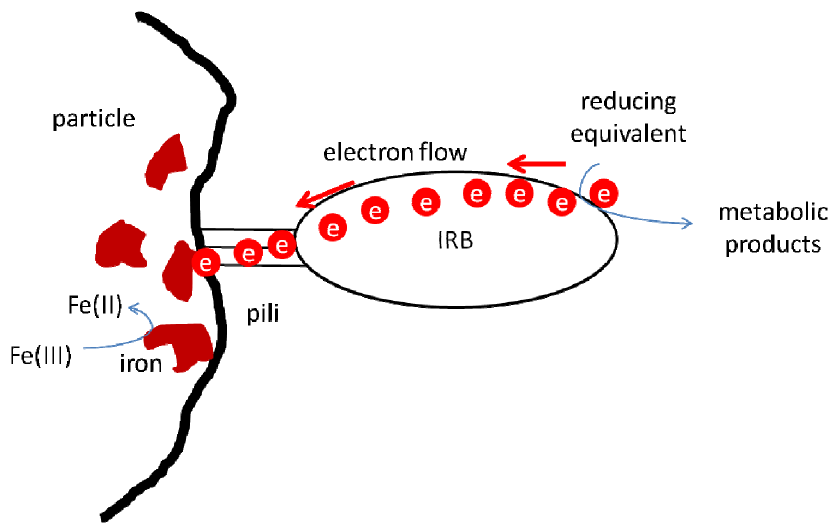

Fig. 1. General life strategy of IRB.

Microbial metal reduction and mineral formation play an important role in the iron and carbon geochemistry and organic matter mineralization in natural subsurface environments. Dissimilatory metal reduction is proposed to be an early form of microbial respiration (Liu 1997). Reduction of metals by bacteria is generally coupled with the oxidation of organic matter (Roh 2003). Therefore, the ability to reduce metals can be exploited not only for the bioreduction or immobilization of many toxic metals, including cobalt, chromium, uranium, and technetium, but also for the biotransformation of organic contaminants to benign products such as carbon dioxide (Fredricson 1997). A number of bacteria with their ability to reduce metal species have been isolated and characterized from different habitats, and many publications have focused on *Shewanella oneidensis* and *Geobacter* spp. (Lovley 1991). The genus *Shewanella* was first described two decades ago (MacDonell 1985). All members of this genus reported so far are facultatively anaerobic, gram-negative, motile by polar flagella, rod-like, and generally associated with aquatic or marine habitats. Although most *Shewanella* species belong to mesophilic, psychrotolerant and psychrophilic bacteria in the *Shewanella* genus have been isolated recently (Zhao 2005). Since a vast majority of the world's surface is covered by oceans, cold deep-sea environments (≤ 4°C) represent a significant portion of potential microbial habitants, and thus, psychrophilic and psychrotolerant *Shewanella* species could be important in the overall biogeochemical processes of metals and carbon (Roh 2006).

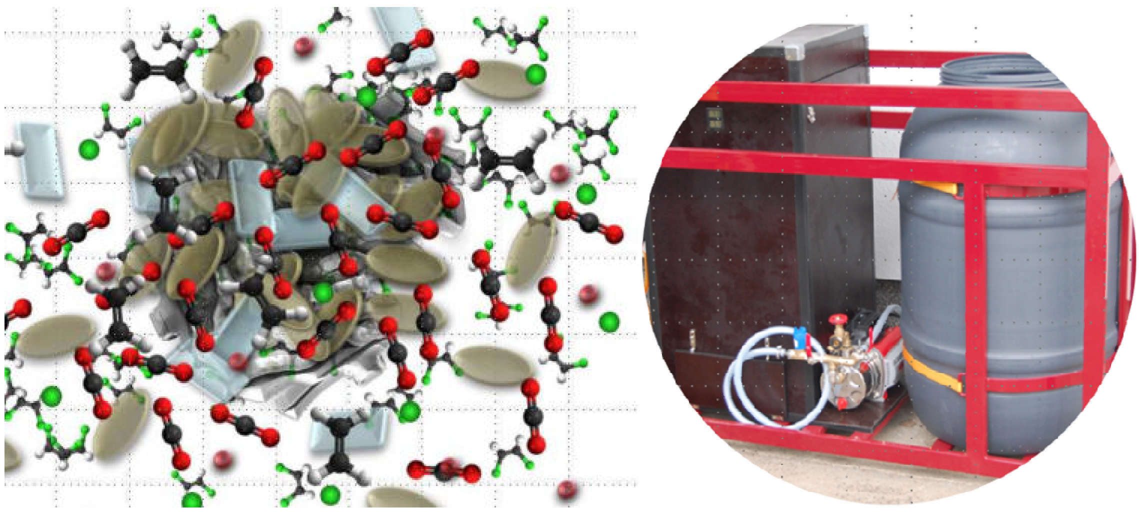

Fig. 2. Engineered application of iron reducing metabolism in contaminated system.

TRAIN TECHNOLOGY

TRAIN treatment technology uses anaerobic microorganisms in fixed-film on iron particles in the form of biofilm to treat groundwater contaminated with volatile chlorinated ethenes. Iron particles are prepared in the working vessel by direct oxidation by aerated water. After oxygen removal, this solution is transferred into the anaerobic reactor and colonized by iron reducing bacteria inoculum which is added under intact conditions (oxygen-free way). Contaminated water is treated by particle suspension which enters into the special application well from anaerobic reactor. Iron reducing bacteria (their consortia) have been evaluated within the reactor. Technological controlling has been doing by respirometric measurement, most probable number (MPN) counting, and fluorescent staining for vitality estimation. The Figure 2 illustrates a schematic view of transformation processes between colonized particles and contaminated system (left) and an illustration of the technical equipment for practical application of TRAIN treatment technology on sites (right).
It is a skid-mounted construction allowing easy transportation and field manipulation. In anaerobic reactor, iron oxides and additional nutrients are added to grow the organisms capable of anaerobic oxidation of volatile chlorinated ethenes. The bacteria degrade these compounds into carbon dioxide, chlorides and ferrous ions and that can be subsequently used to acceleration of vicinal chlorine elimination from ethene molecules. Because of intermediate and competitive inhibition, chlorinated ethene feeding strategies are critical to obtain optimum degradation over the long term. Iron reducing bacteria from particular contaminated soils were tested to determine potential DCE compound degradation. The optimal culture from this testing was isolated and transferred to a bench-scale biofilm reactor, where substrate degradation rates per unit of biofilm surface area were determined. Four pilot-scale biofilm reactors were then established, with feeding strategies and retention times based on earlier testing. Consortium used in TRAIN treatment technology consists from *Shewanella* and *Geobacter* strains which are non-pathogenic and origin from contaminated site where the testing field has been established. This technical solution is protected by two intellectual property rights (CZ28242 and CZ27738).

TESTING SITE

Testing of above described remediation technology was carried out at an area in the Central Bohemia where contamination of groundwater was indicated in the 90th years. Detected contamination was mainly created by chlorinated hydrocarbons (PCE, TCE) and products of their natural degradation. After the detailed investigation of the site and conducting of Risk Assessment the remediation works started at 2013. From geological point of view, the locality is created by sediments of Bohemian Cretaceous Basin. Two important aquifers occur at discussed area. The upper layer is created of Lower Turonian claystones and silty marlstones with less permeability. Static groundwater level is at a depth about 2-3 m below surface. Circulation of groundwater occurs at the depth about 10 m below the surface. Hydraulic conductivity of upper layer of marlstones with fissure porosity approximately described by $K = 5.10^{-7}$ $m.s^{-1}$. Thickness of Turonian layer is about 90 m, general groundwater flow direction is from south to north, the velocity of the groundwater flow is about 30 m per year. From chemical point of view groundwater belongs to the type Ca-Na/HCO_3-SO_4 with excessive hardness and neutral or weak alkaline chemical reaction.

FIELD APPLICATION OF TRAIN TECHNOLOGY

After carrying out of standard clean up approaches – excavation of the centre of contaminated unsaturated zone, *pump & treat* and application of classical *in situ* chemical remediation preparations (lactic acid) a typical development of concentration of chlorinated hydrocarbons (DCE *stall effect*) appeared. In this phase the TRAIN technology in pilot scale was applied.

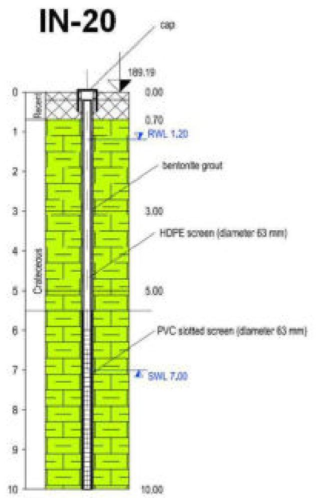

Fig. 3. Diagram of special application well (left) and TRAIN application device at the site (right).

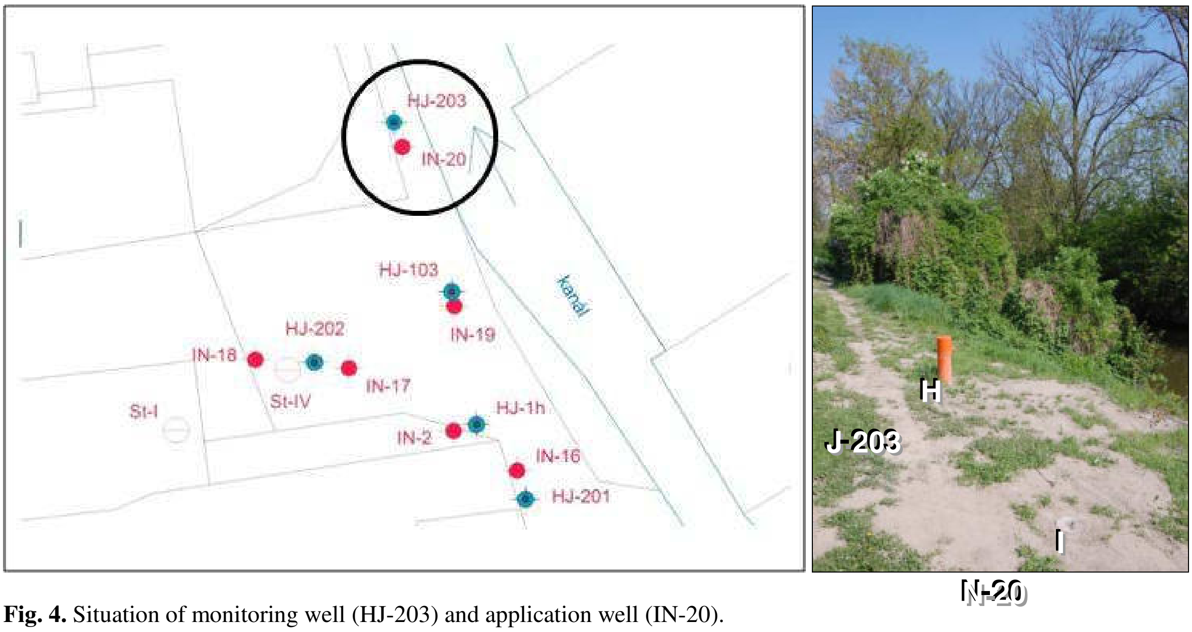

Fig. 4. Situation of monitoring well (HJ-203) and application well (IN-20).

There were drilled several "double boreholes" on the site (Figure 4). The application well is cased in a special way for injection (Figure 3), the monitoring well is a standard borehole with casing PVC 125 mm dia for monitoring of remediation efficiency. Injection of TRAIN suspension was carried out with pressure of about 0,2 MPa. Schedule of applying of TRAIN technology to IN-20 is in the Graf (Figure 5). The samples from well HJ-203 were taken in dynamic way after 10 minutes of pumping 0,02 l/s.

HJ-203 (µg/l)	vinylchlorid	cis 1,2-dichlorethen	trichlorethen - TCE	tetrachlorethen - PCE
26.06.2014	87	4540	2,5	2
07.08.2014	97	2740	5,6	4,5
03.09.2014	169	2260	0,63	0,83
17.09.2014	51	3560	0,99	0,55
07.10.2014	229	2520	0,4	0,83
24.10.2014	259	2430	0,28	0,28
04.11.2014	1360	2210	0,81	0,59
26.11.2014	2290	631	0,63	1
15.12.2014	119	110	1,5	1,5
26.01.2015	13	35	0,21	0,11
25.02.2015	22	66	2,4	2,5
10.03.2015	68	87	0,72	1,5
09.04.2015	97	73	0,63	0,96
17.09.2015	186	315	0,78	0,79
03.12.2015	0	402	4,6	2,5
11.02.2016	30	8,7	0,13	0
06.04.2016	95	449	26	3
20.05.2016	33	72	4,6	1,6

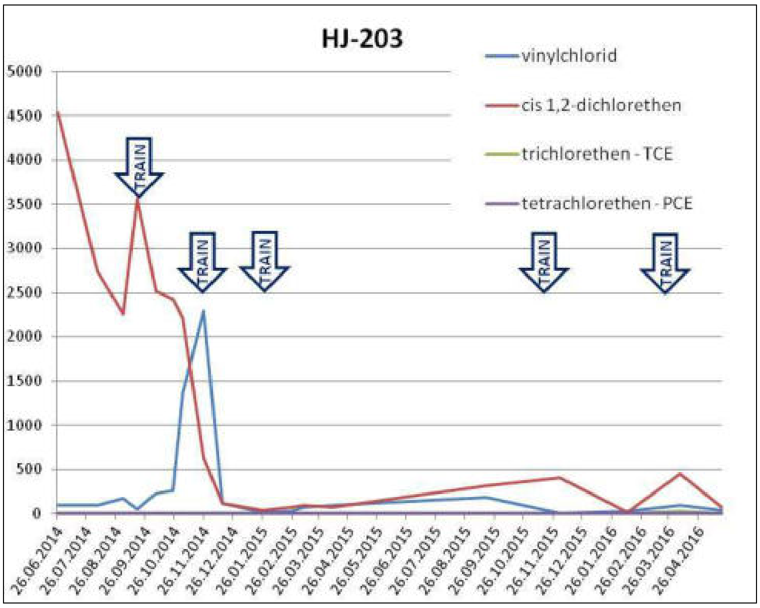

Fig. 5. Results of groundwater monitoring after TRAIN technology application.

RESULTS

Using of the TRAIN remediation technology shows as a very promising and effective approach how to achieve required remediation limits (very often very strict) in concentration of chlorinated ethenes with lower number of chlorine atoms (DCE and VC)

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DEVELOPING PERENNIAL PHYTOTECHNOLOGY FOR CONTAMINATED MILITARY SITE: CASE OF KAMENETZ-PODILSKY, UKRAINE

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KEYWORDS
Miscanthus xgiganteus, abandoned mining site, metals, Ukraine, phytotechnology

ABSTRACT

The semi-field greenhouse experiment on growing *Miscanthusxgiganteus* at the soil from contaminated military site in Kamenetz-Podilsky, Ukraine was done in 2014-2015.The monitoring of translocation of metals: Ti, Fe, Mn, Zn, Pb, As to the plants' tissues: roots, steams, and leaves was completed. Despite high metals' concentrations in the research soil no evident growth inhibition was observed and concentrations of metals in the over surfaceparts were minor. Results confirmed the ability of *M.xgiganteus* to growing at the contaminated military soils. Utilization of the biomass obtained is attractive. The developing phytotechnology is perspective for revitalizationof military contaminated sites at the Eastern Ukraine where military operation is going on.

INTRODUCTION

At the time ofUkrainian Independence, in 1991,military sites included territory of 4500 garrisons, testing areas and military individual sites occupying about 600,000 hectares. In the period between 1991 and 2003, approximately 140,000 hectares of territory, 147 military bases and 507 separate defenseobjects were withdrawn from Ministry of Defense jurisdiction (Analytical Report, 2003). Other has been often operated without any environmental control measures. Currently numerous new military contaminated sites appeared at the Eastern part of the country as result of anti-terroristic operationmainly polluted by metals, oils and products of their decompositions. From that prospective developing technology for abandoned and new military sites revitalization is of great importance for Ukraine.
Taking into account the considerable territory of military contaminated sites and evidenceof their middle or modest contamination (Vygovska, 2006; Nadtogji et al, 2009), application of phytotechnologysounds promising.Sustainable remediation is developing methods that do not require extraordinary resources, or resources better used elsewhere, working with nature, by using supporting natural processes technologies, rather than against it, achieving balance between risk mitigation and the expenditures required to achieve it through optimization based on well-defined criteria (Lesage and Zoller, 2001; Khan, 2005). The union of phytoremediation and production of biofuel crops is perspective approach (Pidlisnyuk,2012)delivering additional benefits -phytoproducts(Trioathi et al, 2016). That method permits to restore marginal contaminated land to agricultural use or urban land bank and simultaneously meet the demand for biomass production as alternative energy sources. The additional request is to stabilize the soil and to decrease maximally extraction of contaminants to the above surface part of the plants to be used for energy production (Pidlisnyuk et al, 2014a).

METHODS AND METHODOLOGY

The contaminated research site waslocated in city Kamenetz-Podilsky, Western Ukraine and had the following coordinates: Latitude-48.680910; Longitude-26.58025. The land was used as a military storage of former Soviet Union Army. The control soil was taken from nearby agricultural field and had the following coordinate: Latitude-48.715954; Longitude-26.577356. The research soil had the next agronomic characteristics pH: 6.90 ± 0.15(in accordance with DSTU ISO 10390-2001 "Quality of the soil, pH"); Nitrogen (nitrates), mg/kg: 11.6 ± 2.3(in accordance with DSTU 4729-2007 "Determination of nitrates and ammonium Nitrogen");Nitrogen (ammonium), mg/kg: 35,2 ± 1,8 (in accordance with DSTU 4729-2007 "Determination of nitrates and ammonium Nitrogen in the soil");Humus (%): 2,84± 0,16 (in accordance with DSTU 4289:2004 "Determination of humus in the soil").Rhizomes of *M. x giganteus*were obtained from the Institute of Bioenergy and Sugar Beat, Ukraine and were one year old at the time of planting. The pot experiment was provided in the greenhouse. There were 7 kg of mixture soil in each pot, and two experiments were done in parallel. In each pot the contaminated soil was mixed with control soil using thenext combinations: 4:0; 3:1;1:1;1:3;0:4. In each pot two rhizomes of *M. x giganteus* were planted. Analysis of heavy metals in the soil, roots, stems and leaves were carried out by Roentgen-fluorescence analysis using analyzer Expert-3L (INAM, Ukraine, http://inam.kiev.us/contact-information). Preparation of samples for analysis was done in accordance with ISO 11464-2001. Statistical evaluation of data was carried out using Microsoft Excel and Statistica software pack at the significance level a=0.05. Extreme values were excluded using the inner-fence test (Altman, 1990).

RESULTS AND DISCUSSION

The long-term investigation has been initiated regarding possibility to use *M. x giganteus* for restoration of former military sites in Ukraine, Slovakia, USA, and Czech Republic (Davis et al, 2014; Stefanovska et al., 2015; Pidlisnyuk et al, 2014b; Pidlisnyuk et al, 2016). This article represents results of initial two years study at the former military site in Ukraine.

Perennial grass *M. x giganteus* is promising plant for use in phytotechnology uniting two processes: phytoremediation and biomass production (Gomes 2012; Nsanganwimana et al., 2014; Pidlisnyuk et al., 2014a).The plantis a sterile inter-specific hybrid of *Miscanthussinensis* and *Miscanthussacchariflorus* (Lewandowski et al, 2015) and belongs to perennial grass with woody stems of heights of 2-4 m. The stems senesce in autumn, but the plant is able to regenerate stems in the spring from its rhizomatous root system. Plant foliage dies at the end of the growing season and can be harvested at high dry matter content. The plant has a C-4 photosynthetic pathway, and has been demonstrated to achieve high light interception and conversion efficiency of C-4 plants, which exceeds that of C-3 crop plants traditionally grown in Northern Europe, by about two-fold (Beale and Long, 1995). Itwas introduced in Europe and exhibited good production properties while used for remediation of brownfield sites, former mining sites and contaminated agricultural lands (Brosse et al, 2012;Nsanganwimana et al., 2015).

Tab.1. Concentration of selected metals in the five variants of soil taken from the research site in Kamenetz – Podilsky, Ukraine (in mg/kg dry weight)

	c [mg/kg dwt]				
	1	2	3	4	5
As	75±5	165±85	115±35	70±0	75±5
Cu	180±10	120±20	125±25	155±5	255±45
Fe	140 955±5 715	135 140±14 580	139 010±13 870	131 530±8 570	136 115±1 515
Mn	5 020±1 580	5 210±40	5 835±115	4 305±375	7 205±1 245
Pb	395±85	185±85	150±50	230±10	450±50
Sr	795±25	935±65	700±10	655±115	1 055±135
Ti	19 815±1 475	17 640±1 370	19 160±1 960	20 265±1 115	19 755±775
Zn	560±30	540±0	515±15	505±15	585±15
Zr	1 910±140	1 515±235	1 165±65	1 070±230	1 115±145

Concentrations of metals in the research soils from Kamenetz-Podilskyare presented at table 1. It can be concluded that soil is rather contaminated by metals, in particular Fe, Mn,Ti and Zr. The monitoring of translocation of Ti, Fe, Mn, Zn, Pb, As to the plants' tissues: roots, steams, and leaves was completed at the end of each vegetation seasons. Results of statistical evaluation of data are presented in table 2. It is obvious that despite high metals' concentrations in the research soil no evident growth inhibition was observed and concentrations of metals in the over surface parts were minor. The coefficient of process effectiveness C was calculated for roots, stems and leaves; coefficient was small for stems and leaves in comparison with roots. The research shows that utilization of the biomass obtained is attractive and can turn the process into a profit making operation. The further research has also to be concentrated on interconnection between *M. x giganteus* biomass quality and quantity, nature and concentrations of contaminants at the military sites including those newly appeared at the East of Ukraine.

Tab. 2. Correlations between metal concentrations in different parts of *Miscanthusxgiganteus* and two sampling periods. Significant correlations (P<0.05) are typed bold red (Pidlisnyuk et al, 2016)

As	*1.*	*2.*	*3.*	*4.*	*5.*	*6.*	*7.*
1. Soil	1,00						
2. Roots – year 1	-0,45	1,00					
3. Stems – year 1	-0,18	0,10	1,00				
4. Leaves – year 1	-0,18	-0,04	-0,11	1,00			
5. Roots – year 2	-0,20	0,00	-0,17	**0,68**	1,00		
6. Stems – year 2	-0,22	-0,02	0,52	-0,16	0,06	1,00	
7. Leaves – year 2	-0,27	0,18	**0,59**	-0,17	-0,07	0,22	1,00
Cu							
1. Soil	1,00						
2. Roots – year 1	-0,31	1,00					
3. Stems – year 1	-0,13	-0,18	**1,00**				
4. Leaves – year 1	0,16	0,05	**-0,29**	1,00			
5. Roots – year 2	0,10	0,56	**0,25**	0,20	1,00		
6. Stems – year 2	0,60	-0,23	**0,40**	-0,03	0,33	1,00	
7. Leaves – year 2	0,47	-0,42	**0,32**	-0,35	-0,20	0,71	1,00
Fe	1.	2.	3.	4.	5.	6.	7.
1. Soil	1,00						
2. Roots – year 1	0,34	1,00					
3. Stems – year 1	-0,44	-0,17	**1,00**				
4. Leaves – year 1	-0,32	-0,66	**-0,14**	1,00			
5. Roots – year 2	-0,68	-0,27	**0,47**	0,18	1,00		
6. Stems – year 2	-0,38	-0,33	**0,67**	-0,09	0,02	1,00	
7. Leaves – year 2	0,01	0,19	**0,31**	-0,48	-0,26	0,62	1,00
Mn							
1. Soil	1,00						
2. Roots – year 1	-0,37	1,00					
3. Stems – year 1	-0,15	-0,46	**1,00**				
4. Leaves – year 1	0,54	-0,57	**0,42**	1,00			
5. Roots – year 2	-0,11	-0,34	**0,10**	-0,01	1,00		
6. Stems – year 2	-0,14	-0,19	**0,78**	0,02	-0,16	1,00	
7. Leaves – year 2	-0,22	0,24	**0,46**	-0,16	-0,57	0,76	1,00
Pb							
1. Soil	1,00						
2. Roots – year 1	-0,30	1,00					
3. Stems – year 1	-0,04	-0,34	**1,00**				
4. Leaves – year 1	0,58	-0,30	**-0,07**	1,00			
5. Roots – year 2	0,33	-0,32	**-0,06**	0,03	1,00		
6. Stems – year 2	0,21	-0,35	**-0,24**	-0,22	0,39	1,00	

7. Leaves – year 2	---	---	---	---	---	---	1,00
Sr							
1. Soil	1,00						
2. Roots – year 1	-0,36	1,00					
3. Stems – year 1	0,08	-0,40	1,00				
4. Leaves – year 1	0,44	-0,66	0,26	1,00			
5. Roots – year 2	-0,15	-0,33	0,26	0,38	1,00		
6. Stems – year 2	0,14	-0,51	0,27	0,28	0,49	1,00	
7. Leaves – year 2	0,49	-0,17	0,10	0,54	0,03	0,46	1,00
Ti							
1. Soil	1,00						
2. Roots – year 1	-0,19	1,00					
3. Stems – year 1	0,38	0,10	1,00				
4. Leaves – year 1	0,19	-0,59	-0,20	1,00			
5. Roots – year 2	-0,17	-0,24	0,30	0,23	1,00		
6. Stems – year 2	0,41	-0,67	0,49	0,18	0,08	1,00	
7. Leaves – year 2	-0,19	0,10	0,19	-0,56	-0,58	0,28	1,00
Zn							
1. Soil	1,00						
2. Roots – year 1	-0,12	1,00					
3. Stems – year 1	-0,06	-0,21	1,00				
4. Leaves – year 1	-0,25	-0,56	0,33	1,00			
5. Roots – year 2	0,52	-0,40	0,17	0,03	1,00		
6. Stems – year 2	0,58	-0,59	0,55	0,37	0,61	1,00	
7. Leaves – year 2	0,83	0,05	-0,02	-0,36	0,21	0,53	1,00
Zr							
1. Soil	1,00						
2. Roots – year 1	0,32	1,00					
3. Stems – year 1	-0,20	-0,27	1,00				
4. Leaves – year 1	-0,62	-0,61	0,16	1,00			
5. Roots – year 2	-0,32	-0,31	-0,14	-0,23	1,00		
6. Stems – year 2	-0,49	0,38	0,23	0,31	-0,44	1,00	
7. Leaves – year 2	0,51	0,52	0,11	-0,67	-0,23	0,09	1,00

CONCLUSION

Two years observation of application developing phytotechnology with second generationbiofuel crop *M. xgiganteus*confirmed a high adaptability of plantto grow at the abandoned metal-contaminated soils such as abandoned military site in Kamenetz-Podilsky, Ukraine. Despite high metals' concentrations in the research soil no evident growth inhibition was observed and concentrations of metals in the over surface parts were minor. The research shows that utilization of the biomass obtained, as an energy resource, is attractive. The proposed phytotechnology is perspective for revitalization of military contaminated sites including those recently appeared at the East of Ukraine.

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BIOLOGICAL CHARACTERIZATION OF CONTAMINATED SITES: ISOLATION OF SOIL FUNGAL SPECIES FROM CONTAMINATED AREAS OF ITALY AND CZECH REPUBLIC TO SELECT TOLERANT SPECIES WITH POTENTIAL IN BIOREMEDIATION OF HEXACHLOROCYCLOHEXANE

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KEYWORDS
Soil fungi, hexachlorocyclohexane, fungal isolation, tolerance, resistance, bioremediation, biotransformation, contaminated sites, persistent organic pollutants

ABSTRACT

Concerning the integration of physicochemical and biological characterization of contaminated sites, the study of soil microbial community represents an important step to shed further light on the environmental contest. To date, the metabolic and morphological versatility of fungi underpins practically all bioremediation applications, but often is still untapped. Fungi play important roles in soil, providing and supporting ecological services for ecosystems and human wellbeing. They can survive in high concentrations of persistent organic pollutants (e.g. pesticides) by possessing mechanisms for the degradation, utilization and transformation of organic substrates. In this research, we have isolated fungal species occurring in samples from sites of Italy and Czech Republic with high concentration of hexachlorocyclohexane. Isolates belonging to Ascomycota, Zygomycota and anamorphic fungi have been identified. Some of them have been reported in literature for the biotransformation of organic pollutants, such as polycyclic aromatic hydrocarbons and pesticides. Moreover, we have investigated the tolerance of selected fungal species to different isomers of hexachlorocyclohexane by using tolerance indices (Rt:Rc, T.I.). For their adaptation to stressful environmental conditions, fungal species isolated from contaminated sites may provide opportunities for new environmentally-friendly, integrated and cost-effective approaches for environmental management and restoration.

Hexachlorocyclohexane (HCH) is a toxic halogenated compound and was included as persistent organic pollutants in the Stockholm Convention in 2008. Its worldwide spread and persistence are considered globally to have severe impacts on human health and ecosystems (Ceci et al., 2015).

Bioremediation mediated by fungi and other organisms is considered to be an environmentally-friendly approach for the detoxification of pollutants, can be integrated to traditional physical and chemical methods, and holds considerable promise for several efficient potential biotechnological applications. Fungi can tolerate extreme environmental conditions and possess extracellular enzymes, many of which are highly potent and relatively non-specific to the chemical composition of the substrate (natural or anthropogenic), and may be induced by nutrient-limiting conditions. These enzymes catalyse a wide range of reactions that can lead to the breakdown of natural recalcitrant polymers, such as lignin, as well as mixtures of xenobiotics including aromatics, organochlorines, and pesticides (Harms et al., 2011).

In this research, we have isolated fungal species occurring in samples from sites of Italy and Czech Republic, contaminated by high HCH concentrations. Fungal isolation was carried out from polluted soil samples using the dilution plate method according to Persiani et al. (2008). The culture medium used was soil extract agar prepared using soil from the sampling area (Maggi et al., 2005).

The analysis of the fungal community of Italian soil samples revealed that the community was rich in species and represented by 38 genera (Ceci et al., 2012). More recently, from the same area we have also isolated and identified 12 anamorphic fungi from soil samples with very high HCH concentrations (5 *Aspergillus* species, 5 *Penicillium* species, 1 *Acremonium* species), and one of these fungi, *Penicillium griseofulvum*, has been studied on its tolerance to HCH and its potential in biotransformation of β-HCH (Ceci et al., 2015). From Czech samples, 63 fungal species were isolated, belonging to Ascomycota, Zygomycota and anamorphic fungi. In the latter case, fungi belong to genera *Aspergillus* (2 taxa), *Penicillium* (13 taxa), *Mucor* (1 taxon), *Trichoderma* (5 taxa) were identified along with several taxa belonging to Sphaeropsidales order, some of them quite rare (Fig. 1).

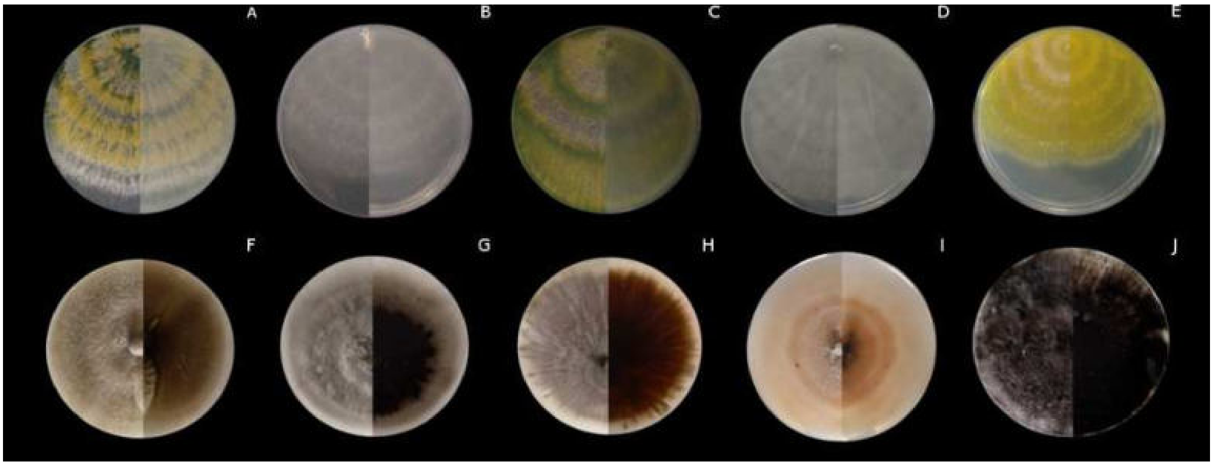

Fig. 1. *Trichoderma* species (A–E) and fungi belonging to Sphaeropsidales order (F–J) isolated from Czech samples. The Petri dishes are shown both from obverse (half circle on the left) and from reverse (half circle on the right).

Some of the isolated fungi from all samples investigated have been reported in literature for their potential in biotransformation of organic pollutants, such as polycyclic aromatic hydrocarbons and pesticides (Ceci et al., 2015; Harms et al., 2011). Moreover, we have investigated the tolerance of 12 selected fungal species from Czech samples to the presence of HCH isomers by using tolerance indices (Rt:Rc, T.I.) (Ceci et al., 2015). Batch tests were performed in Malt Extract Agar medium (MEA, Malt extract 20 g/L, Peptone 1 g/L, Glucose 20 g/L, Agar 20 g/L, Distilled water) for 7 days at 25°C, and a mixture of different isomers of hexachlorocyclohexane (α-HCH: β-HCH: γ-HCH: δ-HCH, 1:1:1:1) were added at the final concentration of 4 mg/L.

Tab. 1. Tolerance indices and pH average values with their standard deviation of the batch tests on fungal tolerance to HCH mixture

Species	Rt:Rc (%)	T.I. (%)	pH Control	pH Test
Cadophora fastigiata Lagerb. & Melin	93±0.2	58.57±0.24	5.14±0.04	5.06±0.01
Harzia acremonioides (Harz) Costantin	81±1.7	85.02±0.15	4.35±0.01	4.90±0.08
Metarhizium sp.	90±0.1	77.01±0.04	4.28±0.12	4.61±0.10
Mucor hiemalis f. *hiemalis* Wehmer	98±0.0	58.13±0.51	3.22±0.08	4.98±0.06
Penicillium daleae K.M. Zaleski	73±0.5	73.74±0.30	4.11±0.17	5.13±0.08
Phialocephala dimorphospora W.B. Kendr.	97±1.7	101.7±1.01	4.75±0.10	4.84±0.02
Sphaeropsidales sp.	110±1.8	76.61±0.48	4.59±0.09	N.A.
Talaromyces sp.	96±1.3	72.60±0.34	4.03±0.14	4.26±0.13
Trichoderma sp. strain 1	100±0.0	85.26±0.04	3.02±0.13	3.83±0.03
Trichoderma piluliferum J. Webster & Rifai	98±0.0	95.06±0.05	4.63±0.03	4.52±0.08
Westerdykella sp.	93±0.6	122.5±0.93	5.66±0.03	5.35±0.12
Zopfiella latipes (N. Lundq.) Malloch & Cain	85±3.3	57.88±0.29	4.78±0.10	4.87±0.03
Malt extract medium	—	—	5.30±0.08	5.21±0.01

All tested fungi showed different tolerance to HCH mixture, and in the majority of the cases tolerance indices are very high (Tab. 1). *Phialocephala dimorphospora*, *Trichoderma* sp. strain 1, *Trichoderma piluliferum* and *Westerdykella* sp. showed the best tolerance. The surface pH was measured in the centre at specific intervals across the diameter of the Petri dish using a portable pH meter. In test conditions, the average pH values resulted in some cases higher than the control ones. Investigations on HCH biotrasformation and the formation of expected metabolites was analysed by gas chromatography-mass spectrometry (GC-MS) according to Ceci et al. (2015). Some intermediates of HCH dehalogenation (e.g. Pentachlorocyclohexene) have been observed and further analyses are in programme to shed further light on fungal biotransformation.

For their adaptation to stressful environmental conditions and for their high performances of tolerance, tested fungal species hold promise for bioremediation applications to contaminated sites and may provide opportunities for new environmentally-friendly, integrated and cost-effective approaches for environmental management and restoration.

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POSTER SECTION

INTERNATIONAL CONFERENCE CONTAMINATED SITES 2016
12 – 13 SEPTEMBER 2016 SLOVAKIA, BRATISLAVA HOTEL BÔRIK

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2	**KATARÍNA PALUCHOVÁ** SLOVAKIA	ESTABLISH THE GEO-DATABASE ON ECOLOGICAL HEALTH OF THE MILITARY SITES
3	***ASSIL NURZHANOVA*** *KAZAKHSTAN*	*REMEDIATION OF SOILS CONTAMINATED BY XENOBIOTICS IN KAZAKHSTAN*
4	**KATARÍNA DERCOVÁ** SLOVAKIA	BIOREMEDIATION OF PCB-CONTAMINATED RIVER SEDIMENTS: ROLE OF AUTOCHTHONOUS BACTERIA AND EFFICACY OF BIOAUGMENTATION ON CONTAMINANT BIODEGRADATION
5	**PETR BENEŠ** SLOVAKIA	LOW-COST COMBINED AEROBIC BIOREMEDIATION
6	**HANA HORVÁTHOVÁ** SLOVAKIA	CHLORINATED BIPHENYLS CONTAMINATION: THE EFFICACY OF BIODEGRADATION USING SINGLE BACTERIAL ISOLATES AND THEIR ARTIFICIALLY PREPARED CONSORTIA
7	***TATYANA STEFANOVSKA*** *UKRAINE*	*CHANGES OF THE SOIL MICROBIAL COMMUNITIES WHILE PLANTING MISCANTHUS X GIGANTEUS AT THE MILITARY CONTAMINATED SITES*
8	**KATARÍNA LÁSZLOVÁ** SLOVAKIA	THE APPLICATION OF BIOSURFACTANTS IN THE BIODEGRADATION OF POLYCHLORINATED BIPHENYLS
9	***MEHMET ÖĞÜT*** *TURKEY*	*MODIFICATION IN COMMUNITY LEVEL PHYSIOLOGICAL PROFILE LEADS INTO INCREASED AVAILABLE PHOSPHORUS IN SOIL RECEIVING BACTERIAL INOCULUM AND ROCK PHOSPHATE*
10	**LUCIE BIELSKÁ** CZECH REPUBLIC	SORPTION AND (BIO)AVAILABILITY OF DDE IN SOILS AMENDED WITH BIOCHAR
11	**LUCIA ŠKULCOVÁ** CZECH REPUBLIC	COMPARISON OF CHEMICAL AND BIOLOGICAL METHODS TO ASSESS AVAILABILITY OF DDE IN SOILS
12	**STANISLAV RAPANT** SLOVAKIA	HISTORICAL MINING AREAS AND THEIR INFLUENCE ON HUMAN HEALTH
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15	**BERTRAND POURRUT** FRANCE	USE OF MULTIPLE BIOMARKERS TO EVALUATE PLANT SPECIES SUITABILITY TO MANAGE CONTAMINATED AREAS
16	**VOJTĚCH TROUSIL** CZECH REPUBLIC	STUDY OF NAPROXEN AND DICLOFENAC REMOVAL IN MODEL AND REAL WATER SAMPLES BY PHOTOCATALYTIC PROCESSES
17	**SLAVOMÍR MIKITA** CZECH REPUBLIC	EXPERIENCES FROM PROFESSIONAL GEOLOGICAL SUPERVISION ON REMEDIATION OF SITE QUARRY SRDCE
18	**ADELINE JANUS** FRANCE	INTEREST OF MISCANTHUS BIOCHARS TO DECREASE THE AVAILABILITY OF METALS IN AQUEOUS SOLUTIONS
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PROJECTS OF THE SLOVAK ENVIRONMENT AGENCY RELATED TO CONTAMINATED SITES

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KEYWORDS
Environmental contamination, Operational Programme 'Environment', investigation, remediation and monitoring of contaminated sites, Environmental Contamination Information System (ECIS)

From 2006 to 2008, an inventory of contaminated sites was conducted throughout Slovakia, establishing the number of likely contaminated sites, confirmed contaminated sites and remediated, reclaimed sites. The 2009 amendment to Act No. 569/2007 Coll. on Geological Works (the Geological Act) as amended incorporated the issue of environmental contamination, at least partially, into Slovak law. In March 2010, the Slovak government adopted a strategic plan for addressing the issue – the National Programme for the Remediation of Environmental Contamination (2010 – 2015). The overarching legal framework is provided by Act No. 409/2011 Coll. on Certain Measures Related to Environmental Contamination and on the Amendment of Certain Acts. Coming into force on 1 January 2012, the Act allows the issue of environmental contamination to be addressed comprehensively, a process that is now in its final phase: projects involving the study, remediation and monitoring of contaminated sites are underway. Given that this is a very costly affair, especially when remediation work is concerned, the primary sources of finances are currently European Union funds.

OPERATIONAL PROGRAMME 'ENVIRONMENT' (2007 – 2013)

The Operational Programme 'Environment' (OPE) was the Slovak Republic's programme document for obtaining aid from European Union funds for the environmental sector from 2007 to 2013. The document was prepared by the Slovak Ministry of Environment in its capacity as OPE Governing Body, and it was approved by the European Commission on 8 November 2007. In terms of budget, it is the second-largest operational programme in Slovakia, with a total budget of over € 2.14 billion.

The overall goal of the OPE is to improve the state of the environment and use resources frugally by finalising and improving Slovakia's environmental infrastructure in accordance with EU and Slovak regulations and by making the environmental components of sustainable development more efficient. This goal is fulfilled via more specific goals, which correspond to the following priority axes and their operational objectives:

- Priority Axis 1: Integrated Protection and Rational Utilisation of Water Resources
- Priority Axis 2: Flood Protection
- Priority Axis 3: Air Protection and Minimisation of the Adverse Effects of Climate Change
- Priority Axis 4: Waste Management
- Priority Axis 5: Protection and Regeneration of the Natural Environment and Landscape
- Priority Axis 6: Technical Assistance
- Priority Axis 7: Creation of a Flood Warning and Forecasting System

Environmental contamination falls under Priority Axis 4: Waste Management, Operational Objective 4.4: Addressing the Issue of Environmental Contamination, Including its Removal. The specific objective of this priority axis is fulfilled by the implementation of three groups of activities, focused respectively on:

- monitoring and investigating contaminated sites and producing hazard analyses
- remediation of the most hazardous contaminated sites
- finalisation of the Environmental Contamination Information System

Within these groups, the following activities can be supported:
Group I: Monitoring and investigating contaminated sites and producing hazard analyses:

A. projects focused on the production of hazard analyses, remediation feasibility studies and inspections of contaminated sites
B. projects focused on the study of high-priority likely contaminated sites

C. projects focused on thorough and repeated investigation of the most hazardous contaminated sites, in line with the established priorities
D. regional studies of the environmental impacts of contaminated sites
E. projects focused on the development of monitoring systems for the most hazardous contaminated sites, in line with the established priorities

Group II: Remediation of the most hazardous sites of environmental contamination:
A. projects focused on the remediation of contaminated sites that present a major hazard to human health and the environment, in line with the established priorities

Group III: Finalisation of the Environmental Contamination Information System (ECIS):
A. implementation of the ECIS as a component of the government's information system
B. preparation of the Atlas of Remediation Methods as a component of the ECIS
C. projects focused on public relations, public awareness and promotion of activities related to the remediation of contaminated sites

Between 2007 and 2013, the Slovak Ministry of Environment made four calls for applications for non-repayable grants (NRGs) as part of Priority Axis 4, Operational Objective 4.4: Addressing the issue of environmental contamination, including its removal. A total of 20 projects were supported, 5 of them were implemented by the Slovak Environment Agency (Tab. 1).

PROJECTS OF THE SLOVAK ENVIRONMENT AGENCY RELATED TO CONTAMINATED SITES SUPPORTED BY THE OPERATIONAL PROGRAMME 'ENVIRONMENT' (2007 – 2013)

Tab. 1. Supported and accomplished projects related to contaminated sites implemented by the SEA (Operational Programme 'Environment' 2007 – 2013)

Project no.	Project title	Project duration	Total eligible expenditure – drawn (€)
1.	**Regionálne štúdie hodnotenia dopadov environmentálnych záťaží na životné prostredie pre vybrané kraje (regióny)** Studies Assessing the Environmental Impact of Contaminated Sites in Selected Regions	10/2008 – 7/2010	319,485.75
2.	**Dobudovanie informačného systému environmentálnych záťaží** Finalisation of the Environmental Contamination Information System	09/2009 – 09/2014	922,733.88
3.	**Osveta, práca s verejnosťou ako podpora pri riešení environmentálnych záťaží v SR** Awareness: Working with the Public to Facilitate the Handling of Environmental Contamination in Slovakia	05/2012 – 08/2015	419,716.04
4.	**Integrácia verejnosti do riešenia environmentálnych záťaží** Involving the Public in Addressing Environmental Contamination	09/2014 – 08/2015	239,694.71
5.	**Štátny program sanácie environmentálnych záťaží 2016 – 2021** The National Programme for the Remediation of Environmental Contamination 2016 – 2021	04/2015 – 12/2015	72,953.00

BASIC INFORMATION ABOUT PROJECTS

1. Project title **REGIONÁLNE ŠTÚDIE HODNOTENIA DOPADOV ENVIRONMENTÁLNYCH ZÁŤAŽÍ NA ŽIVOTNÉ PROSTREDIE PRE VYBRANÉ KRAJE (REGIÓNY)**
STUDIES ASSESSING THE ENVIRONMENTAL IMPACT OF CONTAMINATED SITES IN SELECTED REGIONS

Acronym STUDIEEZ

Main objective of the project
- assess the environmental impacts of contaminated sites in Slovakia's individual regions

Specific objectives	• develop a unified rubric of methods for regional studies of the impacts of contaminated sites in Slovakia • use this rubric to prepare evaluation reports/regional studies for Slovakia's individual administrative regions
Finantial tool	The Cohesion Fund of the European Union within the Operational Programme 'Environment' 2007 – 2013
Project duration	10/2008 – 7/2010
Total eligible expenditure	319,485.75 €
Project code (ITMS)	24140110016
Project manager	Jaromír Helma
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Web	http://www.sazp.sk/public/index/go.php?id=1745

Fig. 1. Environmental Contamination in Predajná, Slovakia

Information and public awareness activities of the project STUDIEEZ (2010) – 2 publications.
Number of accomplished information and public awareness activities of the project – 2.

2. Project title	**DOBUDOVANIE INFORMAČNÉHO SYSTÉMU ENVIRONMENTÁLNYCH ZÁŤAŽÍ** FINALISATION OF THE ENVIRONMENTAL CONTAMINATION INFORMATION SYSTEM
Acronym	DOBUDISEZ
Main objective of the project	• finalise the Environmental Contamination Information System • carry out an informational/educational campaign in the form of regular informational and instructional trainings
Finantial tool	The Cohesion Fund of the European Union within the Operational Programme 'Environment' 2007 – 2013
Project duration	09/2009 – 09/2014
Total eligible expenditure	922,733.88 €
Project code (ITMS)	24140110017
Project manager	Katarína Paluchová
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Web	http://www.sazp.sk/public/index/go.php?id=1746

Fig. 2. The Environmental Contamination Information System – Identification of monitored object via Google Street View service. (Monitored object databases MV – 2A Integrated monitoring of pollution point sources in the vicinity of environmental contamination MI (1989)/Vojany - EVO Vojany – stockpile of inflammables).

Information and public awareness activities of the project DOBUDISEZ (2009 – 2013) – the informational/educational campaign towards state government staff, staff of local governments (regional and municipal), experts.
Number of accomplished information and public awareness activities of the project – 33.

3. Project title	**OSVETA, PRÁCA S VEREJNOSŤOU AKO PODPORA PRI RIEŠENÍ ENVIRONMENTÁLNYCH ZÁŤAŽÍ V SR** AWARENESS: WORKING WITH THE PUBLIC TO FACILITATE THE HANDLING OF ENVIRONMENTAL CONTAMINATION IN SLOVAKIA
Acronym	OSVETA
Main objective of the project	• raise the general public's awareness concerning the issue of addressing environmental contamination, including its remediation
Specific objective	• help the public to be better informed about the issue of environmental contamination
Finantial tool	The Cohesion Fund of the European Union within the OperationalProgramme 'Environment' 2007 – 2013
Project duration	06/2012 – 08/2015
Total eligible expenditure	419,716.04 €
Project code (ITMS)	24140110232
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Fig. 3. The informational and educational meeting with delegates of state government staff, staff of local governments (regional and municipal) and experts engaged in the issue of addressing environmental contamination in Bratislava, Slovakia (13 May 2014, project OSVETA)

Information and public awareness activities of the project OSVETA (2013 – 2015) – 6 publications, 7 films, 2 conferences, 7 courses and meetings, 10 methodical trainings for teachers, 2 school games, 3 school publications, 3 field trips).
Number of accomplished information and public awareness activities of the project – 40.

4. Project title	**INTEGRÁCIA VEREJNOSTI DO RIEŠENIA ENVIRONMENTÁLNYCH ZÁŤAŽÍ** INVOLVING THE PUBLIC IN ADDRESSING ENVIRONMENTAL CONTAMINATION
Acronym	INTEGRÁCIA
Main objective of the project	• promote and involve the wider public in activities relating to environmental contamination, including its remediation
Specific objective	• promote and inform the public about the issue of environmental contamination
Finantial tool	The Cohesion Fund of the European Union within the Operational
Programme	'Environment' 2007 – 2013
Project duration	09/2014 – 08/2015
Total eligible expenditure	239,694.71 €
Project code (ITMS)	24140110300
Project manager	Ing. Zuzana Ďuriančíková
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Fig. 4. Field trip during the training course for university-level instructors and doctoral candidates to the contaminated site Quarry Srdce in Devínska Nová Ves, Bratislava, Slovakia (January 2015, project INTEGRÁCIA)

Information and public awareness activities of the project INTEGRÁCIA (2015) – 2 publications, 1 international conference, 5 courses, 10 methodical trainings for teachers.
Number of accomplished information and public awareness activities of the project – 18.

5. Project title	**ŠTÁTNY PROGRAM SANÁCIE ENVIRONMENTÁLNYCH ZÁŤAŽÍ 2016 – 2021** THE NATIONAL PROGRAMME FOR THE REMEDIATION OF ENVIRONMENTAL CONTAMINATION 2016 – 2021
Acronym	SANÁCIE
Main objective of the project	• work out the National Programme for the Remediation of Environmental Contamination in Slovakia for the period 2016 – 2021
Finantial tool	The Cohesion Fund of the European Union within the Operational
Programme	‘Environment’ 2007–2013
Project duration	04/2015 – 12/2015
Total eligible expenditure	72,953.00 €
Project code (ITMS)	24140110302
Project manager	Katarína Paluchová
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Web	http://www.sazp.sk/public/index/go.php?id=2467

Fig. 5. The integral part of the National Programme for the Remediation of Environmental Contamination 2016 – 2021 are the awareness and informational activities for various group of the general public

Information and public awareness activities of the project SANÁCIE (2015) – 4 press releases, 1 informational meeting with general public.
Number of accomplished information and public awareness activities of the project – 5.

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THE GEO-DATABASE ON ECOLOGICAL HEALTH OF THE FORMER MILITARY SITES IN MONGOLIA

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KEYWORDS
Military sites, database, contaminated sites

For Mongolia, the assessment of contaminated sites, especially due to military related activities, is relatively new. Compared to most western countries, where the structured assessment of contaminated sites has been dealt with since the 1980-1990s, the knowledge and concepts of environmental contamination are scarce in this country. Consequently, prior to the inventory of contaminated lands the introduction of the concepts and international practice on the identification of such territories were evaluated. The review of practices in other countries shows that most countries use a risk model as the basis for the definition of contaminated site and for setting assessment levels for the screening of the concentration of pollutants found in soil and (ground) water. A risk based approach, therefore, also, been the basis for the identification process in Mongolia. Besides former military sites with development of mining and industry the contamination issue is emerging due to the unregulated use of chemicals, even in agriculture. In conclusion, land contamination in Mongolia is a new research subject; however, it needs in systematic monitoring and assessment to reduce potential risk to the population. The results of preliminary site investigation of contaminated sites used under the military propose revealed that in total 6 sites are potentially and 9 sites are probably contaminated. The main types of contaminants were revealed from the laboratory analysis are crude oil, benzene, asbestos and some heavy metals lead, magnesium, sodium, aluminium. About 90 percents of land formerly occupied by military sites are totally covered by construction and demolition waste.

The soil and water contamination issue in Mongolia have risen since 2000s, when the city of Ulaanbaatar experienced a drastic increase of population migration from the countryside. Residential area of the city was planned for population up to $6*10^5$ people, which is currently doubling. At the earliest stage of the soil and water contamination mostly related to the sanitation requirement to ensure the safety of the population living in 'ger' districts[3]. Until 2008, the country has not developed its strategy to mitigate and management of soil and water contamination. The first policy document and related to its implementation, management plan is developed by the Ministry of Environment of Mongolia in 2009, where the Government put a direction to conduct nationwide contamination inventory. The inventory is implemented by different organizations with the support of the international donors. For instance, urban land and water contamination inventory was done in 2010 by the Municipality of UB city with support from the UN, in 2011-2013 in collaboration with Czech Republic the Ministry of Environment is implemented the inventory of contaminated sites due to the mining activities (Burenjargal, Munkhtsengel, 2008).

In 2012 with support from NATO Program on Science for Peace and Security the country is starting inventory of contaminated site due to military activities, focusing on these territories where former Soviet armies are located. The current paper is discussing specifically the process of this inventory and some results from it.

[3] Ger is a traditional dwelling system without sanitary infrastructure and since 2000s this type of dwelling expanded in Ulaanbaatar city.

1. METHODS AND MATERIALS

1.1. Study area

In total 25 Soviet units located in Mongolia during 1950-1990 of which 15 places currently used by Mongolian Armed Forces and the 10 places already transferred to local authorities for civil society use. The selection of pilot project sites was made with the assistance of the Ministry of Defence, Mongolia. The project activities covered major military units which were located along the railway track, due to the region are most populated and potentially exposed to probable contamination.

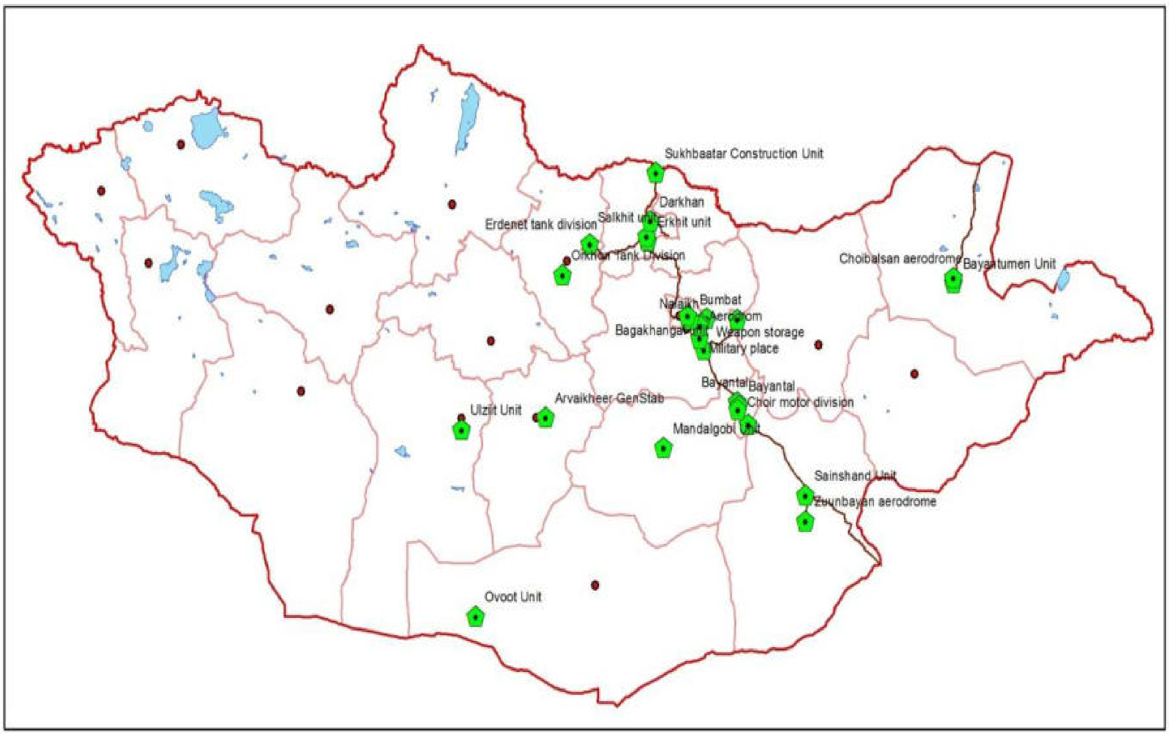

Fig. 1. Location of main military units based in Mongolia during Soviet period (1970-1990).

Most of the military units located along the railways mainly transferred under the jurisdiction of the local authorities. Currently the location, area coverage and facilities used in some of the military sites are under the reconstruction based on archival data left by USSR Military authorities.

1.2. Methods

The review of practices in other countries shows that generic screening levels are commonly used to quickly distinguish sites where threats to human health or the environment are not likely to occur and where no further investigation and assessment is needed. If concentrations in soil and groundwater do not exceed these screening levels, the site does not meet the definition of a contaminated site.

USEPA, Canada and Australia use these generic levels derived with the help of a risk model for different standard forms of land use. The Netherlands only uses screening levels based on the most vulnerable land use. The UK only has screening levels for a limited number of contaminants. The practices from USEPA, Canada and Australia are therefore the most suitable for use in India as they are available for a wide range of contaminant and for different forms of land use.

Therefore, we propose to use the soil quality guidelines from Canada as screening levels in our study. The levels give a sound basis for excluding sites from the process of identifying contaminated sites and are derived for several forms of land uses.

In the most cases, screening levels are well above the natural background levels. The natural background levels of metals and other inorganic chemicals can vary widely and this should be taken into account when applying the assessment levels. Where it can be demonstrated that *natural* background concentrations are elevated (e.g. heavy metal concentrations in mineralized areas), it would be appropriate to develop less stringent assessment criteria. However, care needs to be taken when establishing the level of the natural background and its natural variation as the local background may be influenced by historic mining and/or waste disposal activities. At the end of the identification and assessment process a site can be categorized as shown below using the screening levels and response levels.

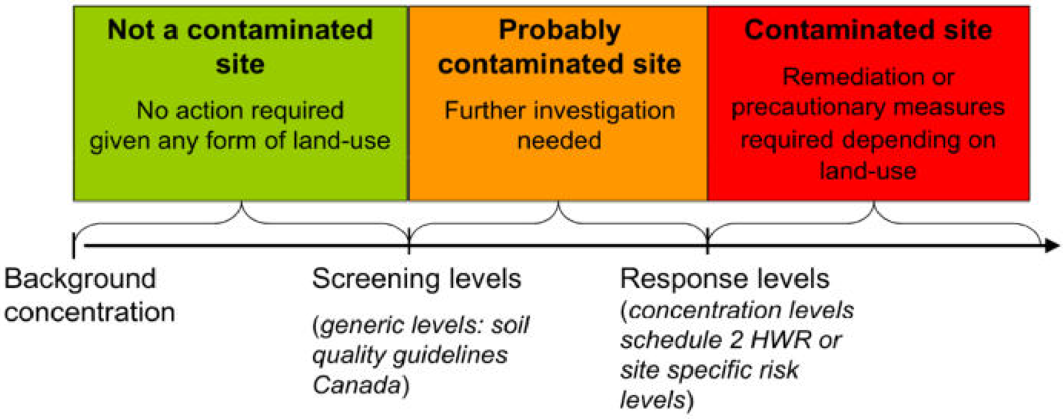

Fig. 2. Work flow of the categorization procedure

The overall approach has followed the following steps:

Step 1. Reconnaissance and Preliminary Assessment of site, including the adjoining areas, through field visits, review of existing documents, maps and literature;

Step 2. Preliminary investigations of the contaminated site and development of conceptual site plan and sampling protocols;

Step 3. Detailed site investigation and characterization;

Step 4. Risk Assessment;

Step 5. Identification of remediation goals/objectives and preparation of Remediation plans.

In this paper, we discuss only the results from preliminary investigation done during the 2013-2015 field seasons. The steps 3 to 5 are under the progress.

2. RESULTS

2.1. Contaminated sites

In total 13 military sites was a subject to preliminary analysis. Due to absence of detailed cadastral maps of military bases for the time of their operation the results of the on-site investigation can't reveal the source types of contaminations. During the preliminary survey for each of the sites totally 14 soil samples were randomly collected besides the control sampling. The samples were located in those places where the visual signs of contamination have present. According to the field survey reports, totally on the territory of Mongolia among the former military sites at 5 places heating plants are destroyed and the crude oil used for the system is spilled in surrounding areas.

Fig. 3. The ruin of old heating plant in Bayantumen soum

Fig. 4. Ruins of buildings in Bayantumen

Fig. 5. Waste refuse dump place in Choibalsan

The social survey for reasons of contamination revealed that mismanagement of facilities left after the former Soviet military union was the main cause of contamination and degradation. To define former land use and reasons of contamination along with the field survey social survey was performed. At the each locations totally 20 respondents were interviewed. The results of the survey summarized as follows:

- According to former military personnel questioned the withdrawal of the Soviet army from Mongolia was planned two years before and planned for the period of 1993-1994 total Armed forces will be withdrawn. The earlier decision was declined by Mongolian Government and during September-November of 1992 all Soviet military forces located in Mongolia force to withdraw. Thus, there were no time limits to arrange cleaning up actions to remove all possible risks related to munitions, operation of heating plants, landfill activities to remove dumpsites etc.
- About 30 % of total respondents related the current environmental status of former Soviet military sites to the economic situation happened during the socioeconomic transition period.
- Most of respondents judged that mismanagement of the sites happened due to Russian official haven't transferred the land to the Government of Mongolia, therefore, these sites were unmanaged for a long time.

The soil and water samplings from surveys military sites were analysed using conventional methods elaborated within the laboratory of Institute Geography and Geo-Ecology. The analysis revealed that the soil layers are mainly contaminated of which topsoil and B zones of pedosphere highly affected.

The main types of contaminants revealed from the laboratory analysis are crude oil, benzene, asbestos and some heavy metals lead, magnesium, sodium, aluminium. About 90 percents of land formerly occupied by military sites are totally covered by the ruins and residues of construction materials. Contamination of a soil by asbestos might critical in places where the residual depth is high. Even though the ruins and construction material doesn't count as contaminants this type of waste has a negative effect on soil fertility, rural development and land reclamation programs.

The content of the revealed heavy metals doesn't exceed maximum allowed concentration mentioned in the Mongolian National Standard System. However, in military sites Ulaan Orkhon, Arvaikheer and Choir exposure to chemicals, namely, sodium salt, sodium formate and aluminium sulphate, caused the death of livestock due to high concentration appearing in soil.

2.2. Geo-database on ecological health

In a framework of this project we also initiated the establishment of the Geo-database on ecological health of the former military sites, which will be an open access data sharing platform for decision makers, policy development as well as for the general public to allow them to monitor actions done by the Government to reduce and mitigate contamination. The Geo-database contains 23 data tables and 195 fields. Each data table is linked with history tables where each transaction will be recorded with actions, time and updated user ID. The database consists of three main datasets of contaminated sites, contaminants and risk assessment. The general data structure is shown in Figure 6.

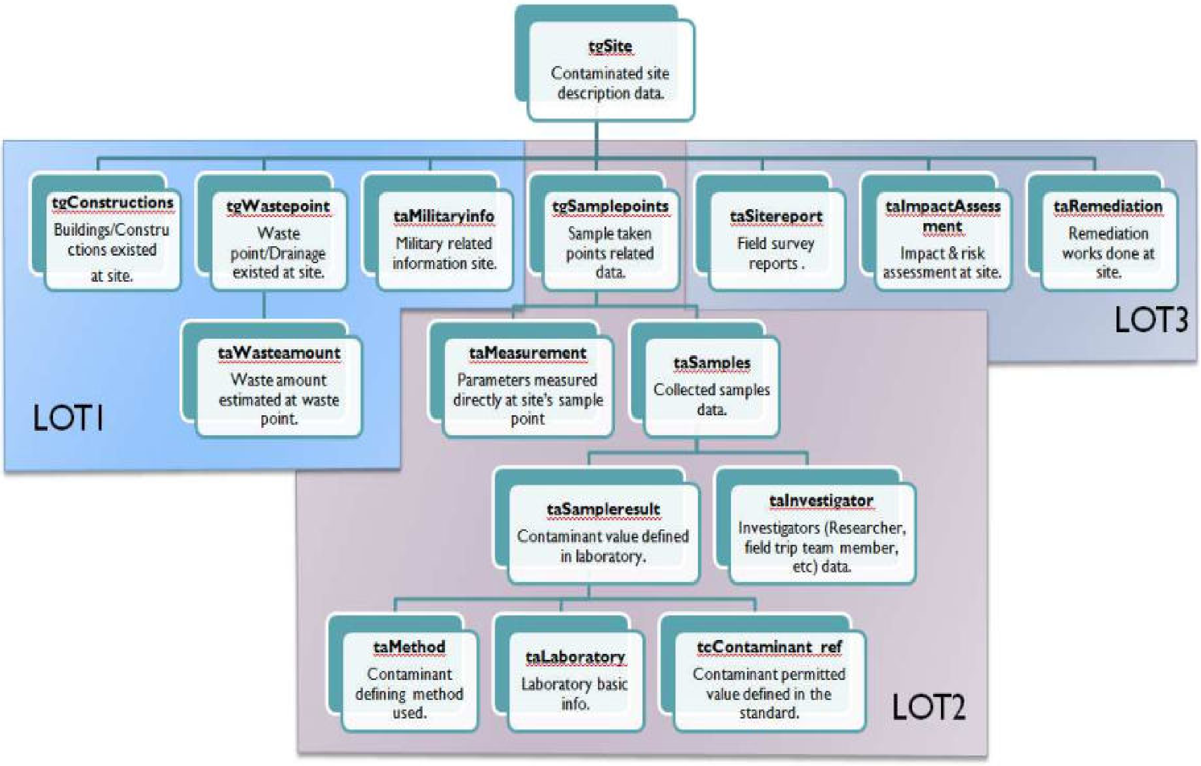

Fig. 6. Data structure

The database has the following subsystems as Data query, Data entry, Map/GIS and Report output.
*Data query***.** Each table data has searching, sorting and displaying interface. In most cases, each data (field) is available to be searched and sorted. The following example demonstrates contaminant searching by name, formula and subject (Figure 7). Data will be sorted by clicking on the field name on top of the table. Browse button displays data in a new window in a more detailed way.

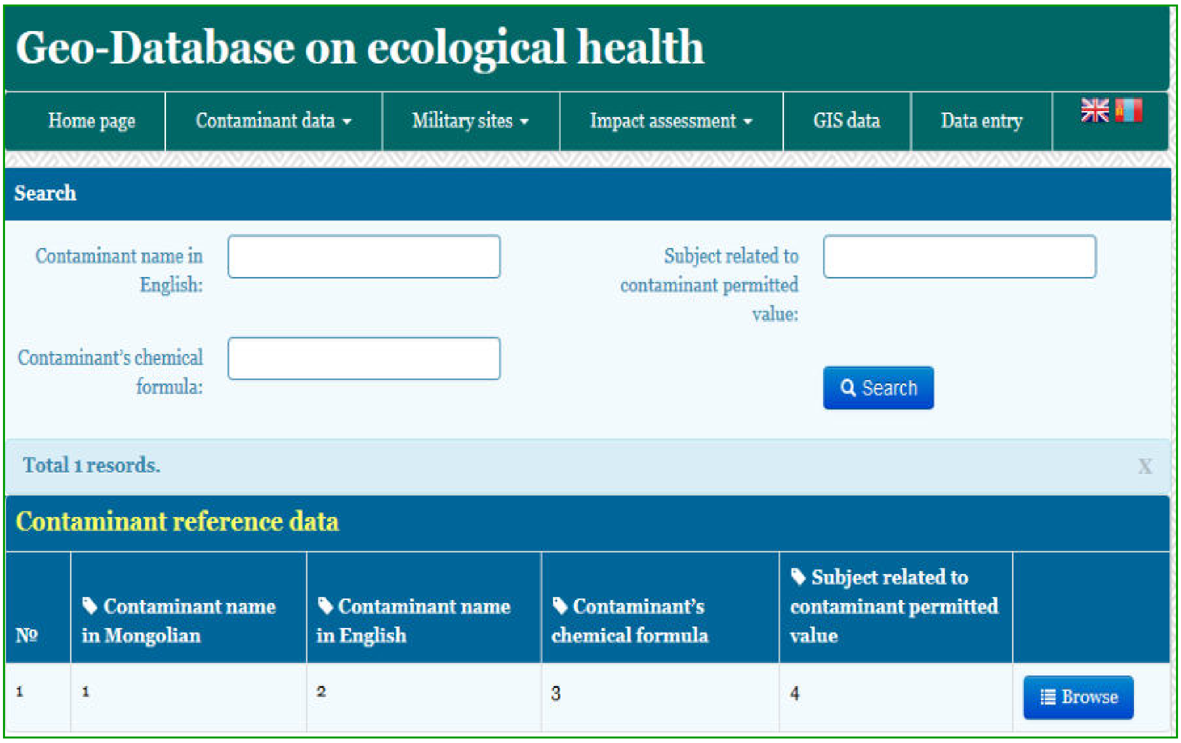

Fig. 7. Data query interface page

Data entering system. Data entry is allowed only for registered users. Therefore user registration module checks and allows users access to system. Each user has limited access, depending their roles in the system. Each action performed by a user is recorded in a transaction protocol file. Data entry form is dedicated for each table. The data entry main interface is presented in Figure 8. List box and check box tools are widely used.

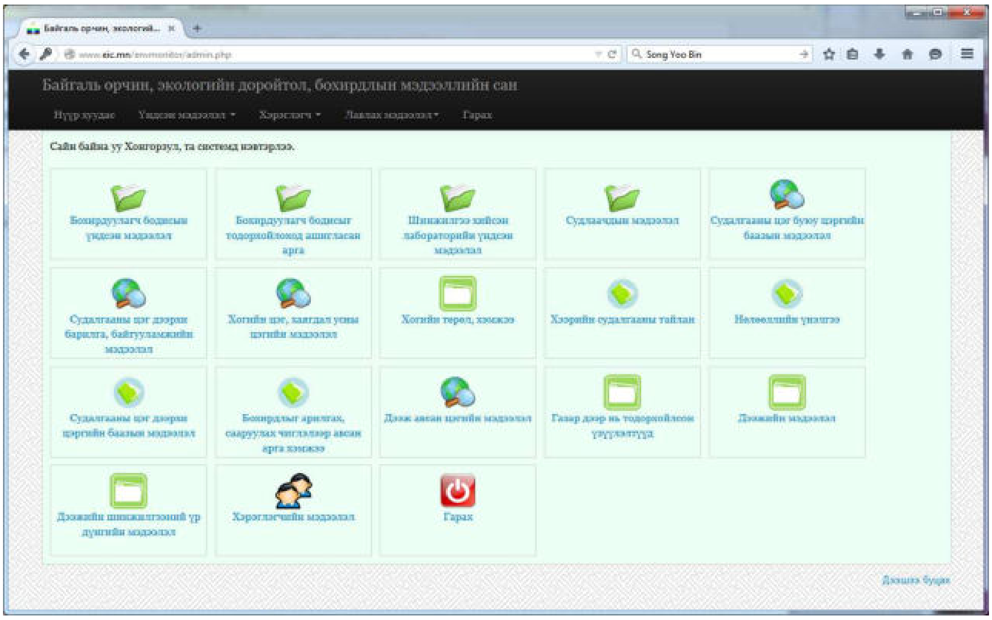

Fig. 8. Data query interface page

Map interface. This interface is assigned to work with map data. The map interface has some additional tools, commonly used for map data such as overlapping layers, retrieving info data by clicking on an interested point and getting attribute data. These tools are presented by icon buttons on top of a map window the under database menu bar. Figure 9 presents an example of the map interface.

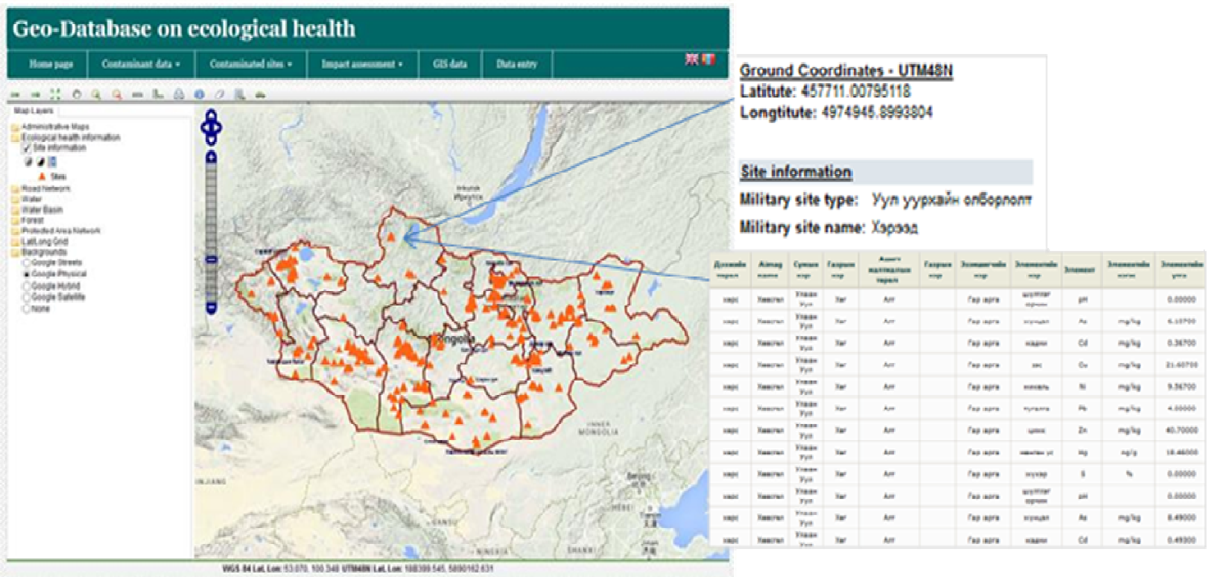

Fig. 9. Map interface page

On top of the main page, there are a menu bar and icons of database tools to be used when interacting with a map such as going back to previous view, zooming, identifying, calculating selected area size, measuring a distance between lines and printing. The left side of the screen is used as the map window to display layers. The metadata or detailed information about a layer is included. These tools/functions can be extended on the user's requirements.

The report output tool allows users to generate reports from database. For instance, it is possible to extract data by selected region, or a report on selected contaminant and contaminated sites.

2.3. Discussion

The results of preliminary site investigation reveal that the contamination levels in/around former military sites exist in a form of hotspots around major infrastructures, e.g. heating plants, waste dumps, construction areas. The major contaminants here are crude oil, benzene, asbestos

The developed open access database is currently new initiative and makes more awareness of contamination it is needed to implement public diplomacy activities. Such works would benefit increase of the local population participates in contaminated site management.

2.4. Conclusion

Mongolia has a widely territory and a low population, which is a primary factor of underdevelopment of the contamination issues in a country. However, recent researches and the results of the current project defines that contamination issue is in a critical situation.

The preliminary investigations made so far identifies that potential risks in currently contaminated sites to the public are high, and thus it is necessary to develop a national strategy on contaminated site as well as implement remediation and restoration activities in those areas where the direct risk to the population has already been defined.

The former military sites in Mongolia experienced an active demolition, however, the proper management of these activities never been implemented, thus increased a risk of contaminant discharge to deeper soil layers and possible to the underground aquifers. Unfortunately, there are no any surveys done in regards to assessment of the underground water contamination. So, it is suggested to implement monitoring activities in critical areas to identify possible risks.

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SPS key priority: Category A3a. Diagnosing the status of contamination by CBRN agents in military sites

BIOREMEDIATION OF PCB-CONTAMINATED RIVER SEDIMENTS: ROLE OF AUTOCHTHONOUS BACTERIA AND EFFICACY OF BIOAUGMENTATION ON CONTAMINANT BIODEGRADATION

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KEY WORDS
Bacteria, bioaugmentation, bioremediation, PCBs, sediments

I. INTRODUCTION

Adverse effects of PCBs on human health are significant and the only one option to avoid them is removing PCBs from the environment. Several methods for PCBs degradation in environmental matrices have been suggested. However, since physical and chemical treatments are generally expensive, currently the research is focused on the development of a less expensive bioremediation treatment. Bioremediation is considered as an efficient, environmental friendly and cost-effective process for elimination of PCBs using microorganisms capable of degrading toxic compounds. The main bioremediation strategies are biostimulation and bioaugmentation [1]. Biostimulation is based on encouragement of growth of the indigenous pollutant-degrading microorganisms using addition of nutrients or inducers of biodegradation. Bioaugmentation is based on the application of indigenous or exogenous microorganisms to polluted hazardous waste sites in order to accelerate the removal of undesired compounds [2]. Bioaugmentation approaches appear to have great potential for remediation of aromatic compounds [3,4]. The study deals with PCB biodegradation in contaminated sediment sampled from Strážsky canal located in the eastern part of Slovakia near Michalovce District. Strážsky canal is part of the factory Chemko Strážske – former producer of commercial PCB products Delor 103, Delor 106, and Hydelor that in total produced approximately 21 500 tons of these products. Although production had been already stopped, surroundings of the industrial Strážsky canal and Michalovce district in particular belong to the most heavily PCB-contaminated areas in the world. Huge amount of waste from the production resulted in serious contamination of soil, sediments, and water in this area [5,6]. Contaminated sediment was chosen for aerobic degradation using bioaugmentation performed by inoculation of sediment by isolated bacterial strains able to degrade PCBs from the same sediment. The strains were added to sediment individually and within the consortia artificially prepared in laboratory. To ensure successful biodegradation, the microorganisms must be present that possess required genes encoding enzyme biphenyldioxygenase responsible for start of the particular degradation metabolic pathway. In our previous study *bphA* gene (chromosomal DNA) was detected in used strains [7].

Objective of this study was a) to assess prospects of bioaugmentation (addition of microorganisms with degradation activities to improve degradation activity of indigenous microflora to degrade PCBs) using the individual bacterial strains (isolates from the autochthonous microflora present in the contaminated sediments) and three consortia artificially prepared as the mutual combination of three single strains (bacterial isolates) in laboratory (finally three pairs of bacteria in the different ratios of inocula 1:1, 1:3, and 3:1); b) to determine kinetics of biodegradation and c) to evaluate ecotoxicity of non-treated and biotreated sediments.

2. MATERIALS AND METHODS

2.1. Bacterial strains and artificially prepared consortia

Bacterial strains with PCB-degradation ability (*Achromobacter xylosoxidans, Rhodococcus* sp., *Ochrobactrum anthropi*, and *Stenotrophomonas maltophilia*) were isolated as described in our previous study [7] from PCB-contaminated sediment. Colony counting during biodegradation: 0.1 ml of medium was diluted in sterile distilled water and applied to Petri dishes with PCA agar. After 48 hour of incubation at 28 °C in the dark, bacterial colonies were counted as colony forming units per ml (CFU.ml^{-1}) using Handy Type Colony Counter (BIO KOBE, Japan). All measurements were carried out in triplicate.

2.2. Characterization of the sediment

Sediment contaminated with PCBs used in the following experiments was collected from the bottom of the sewage Strážsky canal using an Uwitec sampler (Austria) according to the standard protocol in agreement with the Slovak technical norm (STN) in cooperation with the Water Research Institute in Bratislava, Slovakia. Sampling was provided from multiple places mainly to ensure the representativeness of sediment properties (N 48°51´33,8´´; E 21°50´35,4´´Garmin GPSmap 78) pH of sediment was 6.94–7.24, total organic carbon (TOC) was 21.9 $g.kg^{-1}$, redox potential was 197–439 mV, and organic content mass was 1.05–7.06 %. The reference congeners commonly monitored in the environmental toxicology (PCB 8, 28, 52, 101, 118, 138, and 153) were used to represent the PCB contamination and for evaluation of PCB degradation. The total content of the detected PCBs was 30 $mg.kg^{-1}$ of dry sediment.

2.3 Bioaugmentation technique

Bioaugmentation was carried out in 250 ml Erlenmeyer flasks closed with a cotton wool stopper. Twenty g of dried sediment was mixed with 100 ml mineral medium. Four selected bacterial strains and three bacterial consortia were artificially prepared for bioaugmention of sediment. Bacterial strains were prepared individually by incubating in a growth medium at 28 °C and 180 rpm for 48 h. Upon cultivation, bacteria were centrifuged at 3200 rpm for 20 min and the biomass suspension was added into the flasks as inoculum in concentration of 1 $g.l^{-1}$. When the consortia of two bacterial strains were used, concentration of the added suspension of each strain at the ratio 1:1 was 0.5 $g.l^{-1}$. The inocula were applied in three mutual ratios 1:1, 1:3, 3:1. Sediment mixed with the mineral medium free of biomass was used as the experimental control. The flasks were incubated at 28 °C in stationary position for 21 days in the dark. Preparation of sterile sediment: sediment was dried 3 hours at 60 °C.

2.4 PCB extraction and analysis

After the 21 days of biodegradation process, whole flasks content was placed into the centrifugation cuvette. After centrifugation (t=15 min, rpm=3000), the amount of 2 g of dried sediment was placed into Soxhlet extractor and extracted using 60 ml n-hexane for 4 h. After 4 h, a teaspoon of powdered copper was added to the extract and the mixture placed into an ultrasonic bath for 45 min. Copper was removed by filtration through the florisil column. n-Hexane was evaporated on a vacuum rotary evaporator, and the extract was dissolved in 500 µl n-hexane. Internal standard PCB 209 was used for determination of the extraction efficiency, with recovery of 85 %. All determined PCB congeners were analyzed by gas chromatography (GC) using an Agilent 5890A device with an electron capture detector (ECD). Identification of seven PCB congeners (PCB 8, 28, 52, 101, 108, 118, 138, and 153) was based on retention time, while quantitative analysis of the results was performed based on peak areas corresponding to the congeners in the chromatograms. Mixture of seven indicator PCB congeners was used for calibration. Identification of peaks was performed according to [8].

2.5 Evaluation of ecotoxicity before and after biotreatment

Ecotoxicity of PCB-contaminated bottom sediments was studied by aquatic tests using standard water plant *Lemna minor* as the toxicity indicator to monitor the ecotoxic effects of contaminated sediment at the beginning and at the end of the 21 day-bioremediation experiment. The test is based on the monitoring of the growth inhibition of the frond (leaf) number and area. Samples of dried sediment (10 g) after 21 days of cultivation using two bioremediation strategies were placed in a glass pot covered with the Steinberg solution consisting of solutions and ten fronds were placed on the solution level. The pots with samples were cultivated in a box with the temperature of 25 ± 2 °C under special white light (min. 6500 Lux) shining from the top. Parameters for the growth rate inhibition of *L. minor* fronds, Ir, and the biomass growth inhibition of *L. minor* fronds Ia, were monitored at the beginning and then each second day until the 7-th day. These aquatic tests were performed at the Water Research Institute in Bratislava according to (STN EN ISO 20079, 2008).

3. RESULTS

3.1 Bioaugmentation technique

Bioaugmentation using the single bacterial strain

Four bacterial strains isolated from long-term contaminated river sediments collected from sewage of Strážsky canal in eastern part of Slovakia were individually used in separate experimental settings. The degradation capability of single strain was detected in the following order: *Rhodococcus* sp. (70 %), *Ochrobactrum anthropi* (68 %), *Stenotrophomonas maltophilia* (60%), and *Achromobacter xylosoxidans* (31 %).

Bioaugmentation using bacterial consortia

The most effective PCB-degrading consortium in sediment was observed *Rhodococcus sp. + A. xylosoxidans* at the biomass ratio 1:1 (degradation 84 %). Inefficient bioaugmentation at all was observed after application of consortium *O. anthropi + A. xylosoxidans* (41 %) did not exceeded the effectivity of PCB degradation by the individual strain *O. anthropi* (68 %). An experiment in sterile and non-sterile sediment confirmed that natural microflora present in the contaminated sediment enhanced biodegradation and did not inhibit inoculated bacteria.

Monitoring of degradation kinetics by strain *O. anthropi* revealed that major part of degradation occurred during the third week.

3.2 Evaluation of ecotoxicity of non-treated and biotreated sediments

Effectivity of bioaugmentation confirmed sediment toxicity measurement using ecotoxicity biotest with *Lemna minor*. Toxicity of all biotreated sediments with used single strains and consortia was markedly lower than non-treated; toxicity decreased proportionally with degradation of PCBs, it means with diminished PCB concentration as can be seen from kinetics experiment.

4. CONCLUSIONS

Based on the results mentioned above, it can be concluded that bioaugmentation render promising results and lead to a successful bioremediation of the real PCB-contaminated sediments under the laboratory conditions. The highest PCB-degradation using single strain was determined using *Rhodococcus* sp. and bacterial consortium consisted of *Rhodococcus* sp. and *Achromobacter xylosoxidans* (ratio 1:1). The advantage of using a particular consortium when compared with a single strain is a broader range of eliminated PCB congeners (lower and higher chlorinated). The effectivity of bioaugmentation depended on the initially present or inoculated bacteria, their amount and viability. Ecotoxicity of all sediments after the biotreatment in the presence of all consortia and single strains as well, was substantially lower than without treatment. However, during *in situ* degradation process, many other parameters might affect PCB degradation, mainly hydrogeological conditions, that might influence mobility and bioavailability of pollutants. We believe that obtained results could be useful in designing bioremediation technologies for sites contaminated with PCBs.

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LOW-COST COMBINED AEROBIC BIOREMEDIATION

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KEYWORDS
Soil remediation, Low-cost remediation technique, Advanced oxidation processes, BTEX, Chlorinated hydrocarbons, crude-oil hydrocarbons

SUMMARY

Remediation of human impacted environment is often tedious and ineffective. To increase the remediation pace and efficacy, modern chemical and biological methods are used. Chemical processes directly oxidize significant amounts of pollutants, whilst aerobic biodegradation provides environmentally friendly remediation finish. The intersectionof these two approaches is the oxygen! The very oxygen released into environment by chemical oxidation on one side, may subsequently well serve the direct support of aerobic biodegradation. The key factor is the precise combination of the approaches in single functional technique.
Present study investigates low-cost,high efficiency alternativesofO_2 introduction for aerobic bioremediation (LCCAB). The principles focus on targeted application of high oxygen release-potential substances (liquid or solid peroxides) into subsurface, leading to direct contaminant oxidation in the immediate vicinity of application point and consequent support of aerobic bioremediation in greater surroundings. Due to wide range of use aimedat general contamination as well as specific pollutants (such as BTEX, PAH, MTBE, phthalates, or particular forms of nitrogen compound contamination), these innovative low-cost combined technologies have great potential for time and budget limited projects.
Utilization of the described concept provides vital space to remedy environmental burdens even at sites formerly unapproachable for economic or technological reasons.

TECHNOLOGY

The present technology aims to significantly contribute to the innovations within the environmental remediation area. The working protocol will be specified and the application device will be designed for the low-cost alternative technology of highly efficient oxygen supply to the aerobic bioremediation processes performed by verified microbial consortia. The technology is based on the application of substances of high oxygen-release potential, such as liquid or solid peroxides. Liquid peroxides of specific concentrations may be used as oxygen introducers into the contaminated zone through the application bore holes.

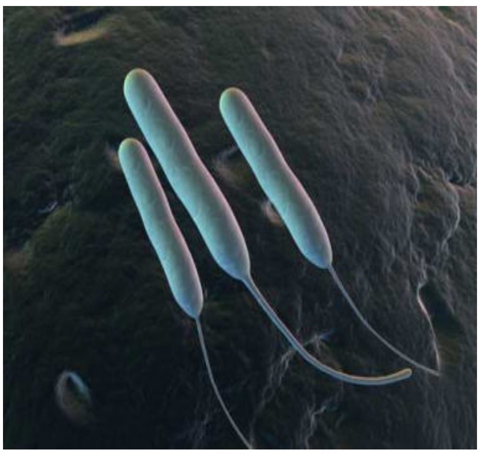

Fig. 1. Aerobic bacteria Pseudomonas

Leaving the bioaugmentation processes aside, two main approaches may be used for the biostimulation of ambient microbial communities:The anaerobic approach, which may prove lengthy due to the character of the metabolic pathway. Or alternatively, the aerobic approach, in which the oxygen serves as a terminal electron acceptor and the target pollutant as a substrate or co-substrate (carbon source). Microorganisms differ significantly by their oxygen affinity, leading to quite variable oxidation-reduction potential preferences.Aerobic microorganisms in the saturated zone prefer the presence of dissolved oxygen, i.e., positive oxidation-reduction potential. The oxygen solubility in liquids is considerably low and further decreases with rising temperature (Henry's Law). Thus, it is crucial to utilize the aerobic microorganism potential for the bioremediation by sufficient supply and distribution of oxygen throughout the entire contaminated zone.

The main objective is to find the suitable processes of alternative oxygen application, so that a synergy is reached between the immediate pollutant oxidation at the close proximity of the injection point and the subsequent pollutant biodegradation by aerobic microbial metabolism within the surroundings. The result is the low-cost intensifying of biological removal of organic (e.g., oil hydrocarbons, BTEX, PAH, chlorinated solvents, MTBE, phthalates, etc...) or inorganic (e.g., some of the varieties of nitrogen compounds contamination)pollutants in the wide vicinity of the application point.The ultimate goal is to design a commercially utilizable device, which will be deployed at a low-cost at appropriate sites, or offered to other parties within the business-to-business cooperation. The thorough knowledge of the active microbial processes is vital to attain the objectives set forth. The analytical support (cultivation as well as molecular microbiology methods) for description, quantification, and vitality/viability verification of the target microbial consortia with great bioremediation potential is the key factor to reach the defined remediation limits.

The following diagram presents descriptive visualization of LCCAB system functions:

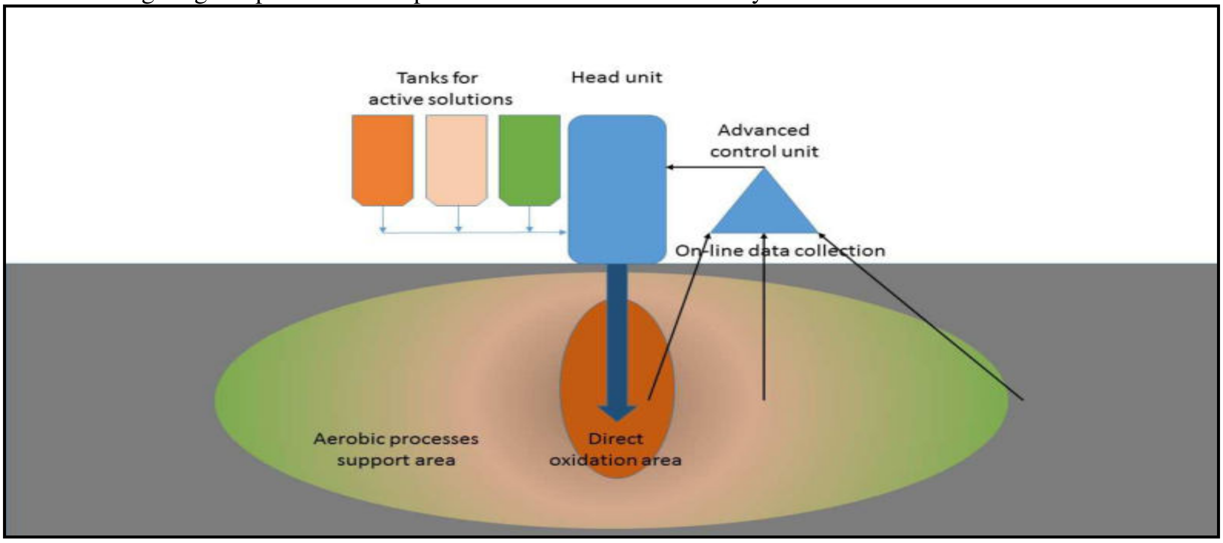

Fig. 2. LCCAB remediation process scheme

The key enabling contribution of this technology will be the significant increase of practical *in situ* aerobic bioremediation applicability due to the changed form and cost reduction. The on-site oxidation intensity control system and the additional nutrient supply option will be implemented for the enhanced two-stage bioremediation support. A new space for environment remediation, even at formerly inapplicablesites, will be opened for aerobic biodegradation. Further, the potential of combining the direct pollutant oxidation with the active introduction of significant oxygen amounts will alter the attitude towards the remediation of substantially complex (the so called difficult-to-treat) sites.

INNOVATION

The innovativeness of this technology is based not only on the targeted cost reduction, but also on the optimization of the original *in situ* enhanced biotechnology principle. The method of low-cost oxygen supply relies in effective and precisely aimed introduction of agents capable to release large amounts of O_2 molecules into the groundwater environment. The main benefit is of economic character: The drastic reduction of the aerobic biodegradation technology costs will allow for its application even at sites formerly inappropriate due to economical unfeasibility.

CONCLUSIONS

The project „Low-cost Combined Aerobic Bioremediation"presents interests of the EPS, s.r.o. company to use its capabilities in the field of science, research, and innovationtoward the design of novel marketable services and productsof environmental biotechnologies.Although the successful introduction of these advanced and environmentally friendly methodsdemands considerable investments in R&D, it unambiguously enforces the stability of the company remediation pillar. Especially due to the capability to offer cost-effective alternatives of standard techniques, the competitiveness of the company on the market is increasing. Consequently, the number of successfully closed remediation projects as well as the overall positive environmental impact are increasing.

CHLORINATED BIPHENYLS CONTAMINATION: THE EFFICACY OF BIODEGRADATION USING SINGLE BACTERIAL ISOLATES AND THEIR ARTIFICIALLY PREPARED CONSORTIA

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KEYWORDS
Bacteria, bioaugmentation, biodegradation, consortia, PCBs, single strains

1. INTRODUCTION

Polychlorinated biphenyls (PCBs) are dangerous substances formed of biphenyl molecule with 1 – 10 chlorine substitutions. The result of long lasting production and application of PCBs – mainly in electrotechnical industry – caused a wide contamination of all ecosystems. The most alarming feature of PCBs is their tendency to bioacumulation in lipidic tissues (Brázová et al., 2012). This is the reason of effort of environmental biotechnologists to remove them from the environment. Some bacterial species, especially those adapted to the presence of PCBs are able to use them as the carbon source. The result of aerobic metabolism initialized by enzyme biphenyldioxygenase are substances with lower toxicity (Murínová and Dercová, 2014). Microorganisms naturally occurring in the soil are forming a wide ecosystem, where the metabolism product of one microbial kind can be used as the substrate for another and they are able to live in synergy. Sometimes, microbes are competing for the substrate, one strain can be predative and repress anothers. This behavior is referred as antagonism. The aim of this study is to find out and subsequently apply the most effective bacterial consortia to the contaminated environment using bioaugmentation approach. From this view, it is important to know the relationships between these bacterial strains.

2. MATERIALS AND METHODS

Biodegradation experiments were carried out in 500 ml Erlenmeyer flasks with 100 ml of defined minimal mineral (MM) medium. The sole carbon source was the commercial mixture of PCBs – Delor 103 added in final concentration 0,1 $g.l^{-1}$. This mixture contains 59 congeners with different degree of chlorination; 7 PCB congeners with mass representation about 30 % of abovementioned PCB product Delor 103 were examinated. Bacterial biomass was added in final concentration 1 $g.l^{-1}$ for single strains and 2 $g.l^{-1}$ for consortia composed of two strains added in biomass ratios 1:3, 1:1 and 3:1. All experiments were performed in duplicate. Bacterial strains were isolated and described in our previous study (Dudášová et al., 2014). Cultivation lasted 6 days on rotatory shaker (180 rpm) at 28°C. Afterwards, residual PCBs were extracted with n-hexane. The PCB extract were analysed by gas chromatograph HP 5890 with electron capture detector. Chromatographs were evaluated according to Mills et al. (2007).

3. RESULTS

3.1 Biodegradation of PCBs by single bacterial strains

Biodegradation abilities of 4 bacterial strains isolated from contaminated sediment were examinated – *Ochrobactrum anthropi, Achromobacter xylosoxidans, Rhodococcus* sp. and *Stenotrophomonas maltophilia*. Biodegradation decreased in the following order: *O.anthropi* – 73 %, *S.maltophilia* – 47 %, *A.xylosxidans* – 41 %, *Rhodococcus* sp. – 40 % (tab. 1).

Tab. 1. Specific growth rates (μ) of bacterial strains and their 50% inhibition concentration values (IC50) of PCB.

Bacterial strain	**Biodegradation of sum of 7 PCB congeners (%)**	**Specific growth rate μ (h^{-1}) with glucose**	**IC_{50} ($g.l^{-1}$)**
Rhodococcus sp.	40	0,063	0,86
Achromobacter xylosoxidans	41	0,120	2,90
Stenotrophomonas maltophilia	47	0,065	0,74
Ochrobactrum anthropi	73	0,018	9,34

3.2 Biodegradation of PCBs by bacterial consortia

Examination of growth of bacterial strains and determination of IC_{50} values of PCBs were the aim of previous studies. Specific growth rates (μ) and IC_{50} values are specified in tab. 1. Based on these findings, we constructed 4 combinations – pairs of bacterial strains. First consortium contained the strains *A.xylosoxidans* + *Rhodococcus* sp.. The strain *A.xylosoxidans* has the highest specific growth rate μ (0,120 h^{-1}). When *Rhodococcus* sp. left its stationary phase, *A.xylosoxidans* was in the middle of logarithmic (log) phase. The second consortium is composed of strains *Rhodococcus* sp. and *S.maltophilia*. When *Rhodococcus* sp. was already in the end of stationary phase, *S.maltophilia* entered the log phase. Both strains has the similar values of specific growth rate and IC_{50} of PCBs. The strains forming the third consortium, *A.xylosoxidans* and *S.maltophilia* were entering the log phase in the same time. The last consortium, combination of *O.anthropi* and *A.xylosoxidans* has been chosen due to their higher resistance against PCBs (IC_{50} values: *O.anthropi* 9,34 $g.l^{-1}$ and *A.xylosoxidans* 2,90 $g.l^{-1}$).

***Rhodococcus* sp. + *A.xylosoxidans*.** We observed 62 % removal of PCBs if strains added in biomass ratio 1:3 (excess of *A.xylosoxidans*), representing 21 % increasment of biodegradation in comparison with both single strains. The ratio 3:1 (with excess of *Rhodococcus* sp.) was less effective. Congener PCB 8 was the best degraded (nearly 80 %). *Rhodococcus* sp. is an early-growing strain with early-onset death phase of the growth and it probably didn´t consumes all nutrients, therefore, they were available for the late growing *A.xylosoxidans*.

***Rhodococcus* sp. + *S.maltophilia*.** This combination of bacteria removed 69 % of sum of the PCB congeners if strains added in biomass ratio 1:3 (excess of *S.maltophilia*), representing 22 % increasing in biodegradation in comparison with *S.maltophilia* and 29 % with *Rhodococcus* sp.. Both strains has the similar μ and IC_{50} values. Biodegradation of PCBs with unequal biomass ratios (1:3 and 3:1) were almost the same (69 % and 66 %). It is possible, that the metabolites of *Rhodococcus* sp. have toxic effect on *S.maltophilia*. That is visible especially in biomass ratio 1:1 (only 47 % of degraded PCBs). When *Rhodococcus* sp. is in minority, its metabolites are in lower concentration and their impact is not significant. Higher biodegradation of PCB congeners with high degree of chlorination (pentachlorinated congeners PCB 101 – 71 %, PCB 118 – 65 %; hexachlorinated congeners PCB 153 – 50 %, PCB 138 – 59 %) is the key finding.

***S.maltophilia* + *A.xylosoxidans*.** As with the second consortium, antagonism if strains added in equal biomass ratio (1:1) was observed. This equal-biomass consortium was less effective than both single strains. Biodegradation was successful only if strains were added in unequal ratio, 54 % removal of PCBs was achieved – 7 % increasing in comparison with *S.maltophilia* and 13 % with *A.xylosoxidans*. Logarithmic phases of growth of these strains are synchronized, so there is an suspection they compete for the substrate. When one strain was in excess, it overgrew the second one and led the biodegradation process.

***O.anthropi* + *A.xylosoxidans*.** Regarding biodegradation of PCBs, the fourth consortium has shown to be less effective. In the previous combinations, biomass added in unequal ratio exhibits higher biodegradation percentage, this consortium is an exception. If biomass was added in ratio 1:1, 58 % of PCBs were removed. This consortium is still about 15 % less effective than single strain *O.anthropi*; but 18 % more effective than single strain *A.xylosoxidans*.

4. CONCLUSION

Based on the results mentioned above, it can be concluded that use of bacterial consortia is in most cases more effective in PCB degradation than application of single strains. Although, sometimes the antagonism is observed, in every combination it´s possible to find out some biomass ratio showing better biodegradation by consortia than by single strain. The most effective single strain is *Ochrobactrum anthropi* (73 %). Surprising that the least effective consortium also contains this strain, in combination with *A.xylosoxidans*. Although 58 % of PCBs are removed, in the context of the comparison it´s not sufficient. For elimination of highly chlorinated PCB congeners, application of consortium *Rhodococcus* sp. and *S.maltophilia* in unequal biomass ratio seems to be the best one. Nearly 70 % PCBs were degraded by consortium with excess of *S.maltophilia*. It is also the most efficient consortium of all. In the following research we would like to apply the best consortia to the real contaminated sediment using the approach known as bioaugmentation.

ACKNOWLEDGEMENT

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THE APPLICATION OF BIOSURFACTANS IN THE BIODEGRADATION OF POLYCHLORINATED BIPHENYLS

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KEYWORDS
Bacterial strains, biodegradation, biosurfactants, polychlorinated biphenyls

INTRODUCTION

Polychlorinated biphenyls (PCBs) are hazardous, persistent environmental contaminants strongly bound to soil 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. PCBs were produced in Czechoslovakia by chemical plant Chemko in Strážske until 1984. Nowadays, Eastern Slovakia belongs to the most PCB contaminated areas in the middle Europe. Bioremediation is considered as an efficient and cost-effective process for the decontamination of PCBs (Tandlich et al., 2011). It may involve bioaugmentation and/or biostimulation strategies as the introduction of PCB-degrading bacterial strains individually or as a consortium and introduction of nutrients and oxygen (Mrozik and Piotrowska-Seget, 2010). Several microbial strains isolated from environmental samples, both Gram-negative (mainly of the genera *Pseudomonas*, *Burkholderia*, *Comamonas*, *Cupriavidus*, *Sphingomonas* and *Acidovorax*) and Gram-positive bacteria (predominantly belonging to the genera *Rhodococcus* and *Bacillus*), are nonetheless able to degrade PCBs (Pieper and Seeger 2008). To stimulate the degradation abilities of bacterial strains, several inducers have been proposed. Promising method seems to be induction of aerobic biodegradation using biphenyl and solubilisation of hydrophobic and low soluble PCBs in the presence of surface active agents. Biosurfactants are amphiphilic compounds produced by various microorganisms, mostly bacteria. The use of biosurfactants for enhanced elimination of pollutants from soil and water was found to be an eco-friendly approach and also alternative to less or no degradable synthetic surfactants. This work describes stimulation of bacterial aerobic biodegradation of PCBs in the presence of biosurfactant rhamnolipid.

MATERIAL AND METODS

PCB-degrading bacterial strains *Achromobacter xylosoxidans, Stenotrophomonas maltophilia* and *Rhodococcus* sp. isolated from long-term contaminated area in surroundings of the former producer of PCBs Chemko Strážske and indentified according to Dudášová et al. (2014) were used in these experiments. PCB degradation was determined using the commercial PCB product DELOR 103 (Chemko Strážske, Slovakia).

Bacterial inocula were prepared by growing the cultures according to Dudášová et al. (2014) on a rotary shaker 180 rpm for 48 h at 28 °C. Biomass was harvested by centrifugation, added to 100 ml of MM medium at a final concentration of 1 $g.l^{-1}$. The composition of MM medium has been described by Dudášová et al. (2014). DELOR 103 was added to each flask as solution in DMSO at a final concentration of 100 $mg.l^{-1}$. Rhamnolipids were added to the MM medium at a final concentrations 0.02 $g.l^{-1}$, 0.50 $g.l^{-1}$, 0.10 $g.l^{-1}$ and 0.20 $g.l^{-1}$. Biodegradation of PCBs by bacterial strains was carried out in 500 ml Erlenmeyer flasks equipped with glass columns filled with SILIPOR C18 sorbent and closed with a cotton wool stopper. The apparatus has been described previously (Vrana et al., 1996). Flasks were incubated at 28 °C on a rotary shaker for seven days.

PCBs were extracted from the liquid phase of the medium twice with n-hexane. The samples were analyzed by gas chromatography GC (Agilent 5890A) with an electron capture detector (ECD). The GC conditions were as follows: silica capillary column (30 m × 0.25 mm i.d.) with non-polar stationary phase HP-5MS (0.25 µm), and column temperature program: initial temperature 70 °C (hold 2 min) to 150 °C at 25 $°C.min^{-1}$ (hold 0 min), from 150 °C to 200 °C at 3 $°C.min^{-1}$ (hold 0 min), from 200 °C to 280 °C at 8 $°C.min^{-1}$ (hold 3 min); carrier gas H_2 (90 kPa) with constant flow 1.5 $ml.min^{-1}$; injection temperature: 250 °C ; injection volume: 2 µl using split injection mode (split time: 2 min), detector: ECD, 280 °C, make up gas N_2 40 $ml.min^{-1}$. Identification of peaks and their calibration were performed using standard mixture of the six indicator and three other PCB congeners - PCB8 (2,4'), PCB28 (2,4,4'-), PCB52 (2,2'5,5'-), PCB101 (2,2,4,5,5'-), PCB118 (2,3',4,4',5-), PCB138 (2,2,3,4,4,5-), PCB153 (2,2',4,4',5,5'-), PCB180 (2,2,3,4,4,5,5'-), PCB203 (2,2,3,4,4',5,5',6-) and biodegradation was then calculated (Mills, 2007).

RESULTS AND DISCUSSION

Biogedradation of PCBs by bacterial strains

The purpose of this study was to compare the influence of microbial surfactant rhamnolipid on the PCB-degradation using three bacterial isolates. All bacterial strains originated from the long-term PCB-contaminated sediments of Strážsky canal. Bacterial strains *Achromobacter xylosoxidans*, *Rhodococcus* sp. and *Stenotrophomonas maltophilia* were cultivated under various conditions with the addition of different concentrations of exogenous commercial product rhamnolipid to mineral medium artificially spiked with PCBs. Degradation of PCB-congeners confirmed that addition of rhamnolipid increased the biodegradation of PCBs by gram-negative bacterial strains *A. xylosoxidans* and *S. maltophilia*. On the contrary, rhamnolipid decreased the biodegradation ability of gram-positive bacteria *Rhodococcus* sp. against the control (without rhamnolipid addition). The effect of rhamnolipid on total PCB degradation by *A. xylosoxidans* depended on the concentration of added rhamnolipid. Increasing rhamnolipid concentration (0.02-0.20 $g.l^{-1}$) increased the biodegradation from 38% to 68%. In the case of *Rhodococcus* sp. the rhamnolipid addition decreased the biodegradation from 60% to 42%. The highest degradation was observed in the case of lower chlorinated congeners (PCB8, PCB28) by strain *A. xylosoxidans* in the presence of rhamnolipid 0.10 and 0.20 $g.l^{-1}$.

Bacterial growth

The number of viable bacterial cells in experiments under various conditions (addition of different rhamnolipid concentrations and PCBs) was monitored using the drop plate method. In the case of *A. xylosoxidans* and *Rhodococcus* sp. no growth was observed after 7 days of incubation. The counts of viable cells was significantly lower after the incubation than at the beginning. On the contrary, in the case of bacterial strain *S. maltophilia* the rhamnolipid addition stimulated the growth of viable cells.

CONCLUSIONS

The addition of biosurfactant rhamnolipid increased the biodegradation of PCBs by Gram-negative bacterial strains *A. xylosoxidans* and *S. maltophilia*. Rhamnolipid addition caused inhibition of the PCB-biodegradation only in the case of gram-positive strain *Rhodococcus* sp. Results obtained in this work indicate that rhamnolipid addition at various concentrations together with PCBs lead to the stimulation of the bacterial growth and higher biodegradation of PCBs using Gram-negative bacterial strains. It was confirmed that bacterial strains *A. xylosoxidans* and *S. maltophilia* are suitable degraders, able to degrade about 60% of the initial amount of PCBs. The bioaugmentation using bacterial strains with required degradation ability, and amendment using rhamnolipid to solubilize hydrophobic PCBs is considered as one of possible approaches for increasing biodegradation of dangerous organochlorine pollutants from contaminated site.

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SORPTION AND (BIO)AVAILABILITY OF DDE IN SOILS AMENDED WITH BIOCHAR

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KEYWORDS
Biochar, sorption coefficient, DDE, polyethylene passive sampling, remediation

ABSTRACT

Soil serves as a sink for persistent, bio-accumulative and toxic pollutants that may accumulate in soils to high levels and, thus, present a substantial challenge for environmental risk assessment/ management. Moreover, soil quality has been found to decrease particularly due to the increasing presence of contaminants resulting from both intentional use of chemicals (e.g., pesticides) as well as unintentional contamination from diffusive sources (such polycyclic aromatic hydrocarbons from traffic). Two main pressing issues for soil management can be, therefore, indentified as the development of effective but cheap remediation strategies and the improvement of soil quality. Addition of biochar to soils may potentially help in solving both problems.

Fig. 1. Wood-derived biochar during grinding

Fig. 2. Rice husk-derived biochar during sieving

Soils contaminated with *p,p´*-DDE (the main degradation product of the formerly intensively used pesticide *p,p´*-DDT) represent old burdens worldwide that have to be effectively managed to avoid environmental and health hazards. In this study, biochar (BCH) addition to soil has been suggested as an effective tool for managing o contaminated sites. BCH role in controlling risks of *p,p´*-DDE was assessed i) in the presence and absence of soil by means of the batch equilibrium method and passive sampling, ii) at various BC-to-soil ratios and, iii) for two types of BCH (rice husk- vs. wood-derived). Sorption coefficients (log K_d values) measured for *p,p´*-DDE and the two tested BCHs were 1.4-times higher than for the soil and showed a higher degree of non-linearity suggesting that BCHs are more effective sorbents at lower concentrations. Addition of BCH to soil significantly decreased availability of *p,p´*-DDE (i.e., *p,p´*-DDE porewater concentration measured by polyethylene sheets as passive samplers) and this effect was apparent even at a low BCH dose (1%). Sorption of *p,p´*-DDE further increased with increasing BC contents in soil (tested up to the level of 20% of BC) but the trend was not linear. The two tested BCHs revealed similar affectivity in sorption of *p,p´*-DDE. Thus, the origin of BCH can be considered less important than its dose. The results suggest that BCH can effectively sequester contaminants in soil, thus providing a promising tool for remediation of contaminated sites.

Fig. 3. A biochar-soil slurry with the PE-sheet as a passive sampler

COMPARISON OF CHEMICAL AND BIOLOGICAL METHODS TO ASSESS AVAILABILITY OF DDE IN SOILS

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KEYWORDS
Bioavailability, bioaccumulation, earthworms, DDE, passive sampling, XAD, SPME, HPCD

ABSTRACT

Due to the wide range of structural features and sorption – relevant properties, soils are natural reservoirs for the hydrophobic organic contaminants including organochlorine pesticides such as *p,p´*-dichlorodiphenyl dichloroethylene (*p,p´*-DDE). Due to its high hydrophobicity (log Kow 6.5), DDE tends to be strongly bound to soil and this sorption promotes with increasing DDE-soil contact time (i.e. aging). Thus, for the aged DDE, the risks assessed on the basis of the total soil concentration would overestimate the actual risks to biota due to the partial unavailability of aged DDE to be taken up by an organism. Generally, two approaches can be used to measure the potential availability of contaminants from soil: biological methods and their alternatives of chemical extraction and passive sampling based techniques. However, using of various chemical methods results in distinct differences in a predicting of biological uptake. Therefore, the present study was designed to follow the strategy of combining various methods of mild extraction as well as passive sampling techniques to assess their potential to predict bioavailability to the earthworms.

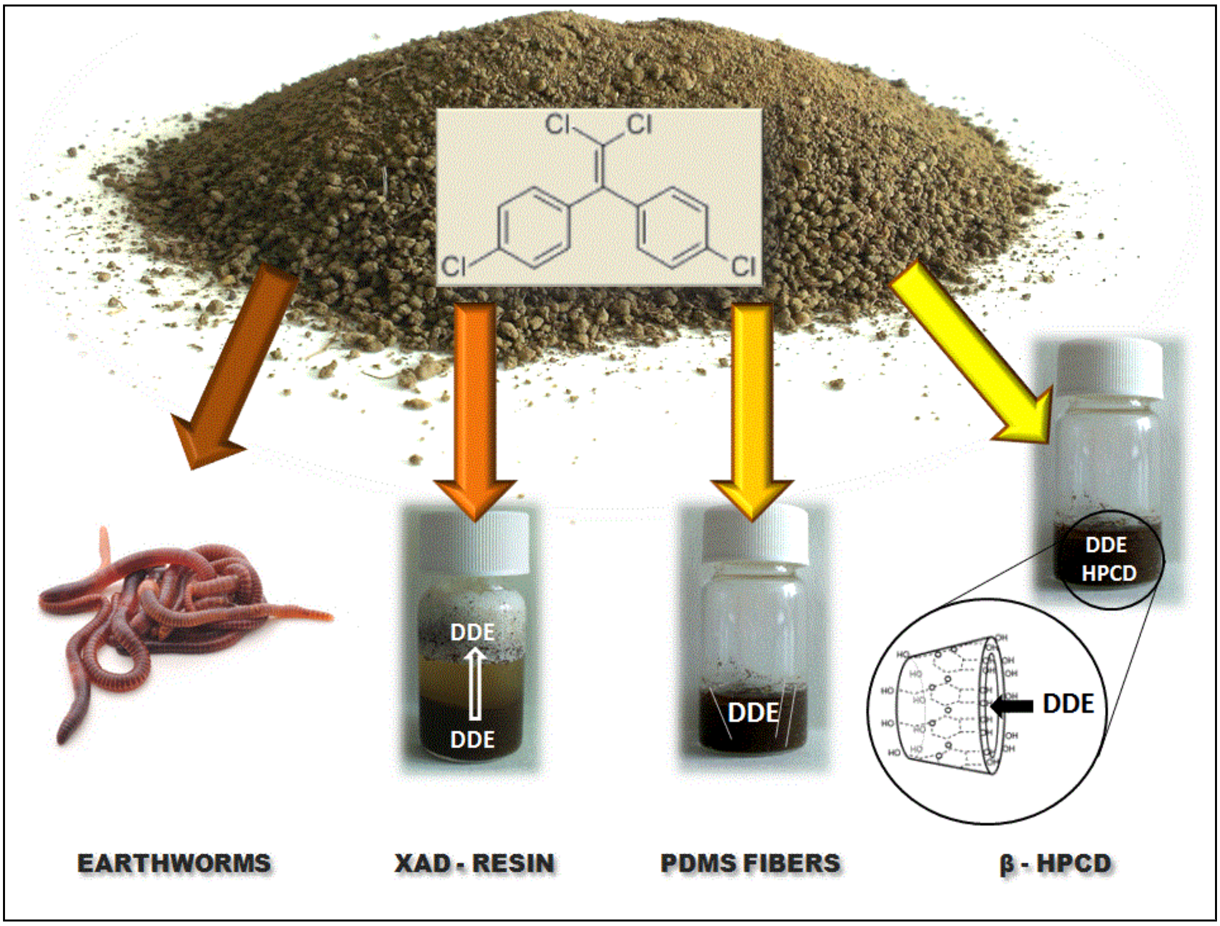

Fig. 1. A graphical presentation of the experimental design including methods employed in the assessment of *p,p´*-DDE chemical and biological availability in soil

The study compared the ability of XAD resin, ß-cyclodextrine, and PDMS-fibers to mimic earthworm uptake from a historically (> 40 years) and a laboratory contaminated soils, thus representing two extreme scenarios with regard to the length of pollutant-soil contact time. The extent of bioaccumulation to earthworms was estimated at fixed exposure periods (10, 21 and 30 days) and at equilibrium derived from uptake curves by kinetic modeling. The kinetics for uptake into passive samplers were then measured over a period of 30 days.
As the most reliable chemical predictor was found XAD presumably because of the combined skin and gut exposure of earthworms to DDE often observed for compounds with log K_{ow} > 5. The observed poorer predictability of SPME may be, on the contrary, related to its inability to consider the uptake realized by other pathways but skin leading to the underestimation of the aged DDE. As the poorest predictor of earthworm uptake appeared to be HPCD in our study. Concluded, the degree of predictability seems to be associated with the capability of the chemical method to mimic the earthworm uptake via skin and intestinal tract as well as with the insufficient length of exposure time.

HISTORICAL MINING AREAS AND THEIR INFLUENCE ON HUMAN HEALTH

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KEYWORDS
Historical mining areas, potentially toxic elements, health indicators, health status

ABSTRACT

Impact of potentially toxic elements (PTE) on the health status of population of the Slovak Republic has been studied in two historical mining areas with or extraction from Middle Ages (the Middle Slovak Neovolcanics, the Slovak Ore Mts.) and one historical mining area with more than hundred years brown coal mining (Upper Nitra region).
The contents of PTE were analysed in groundwater/drinkingwater and soils. The health status of resident population was evaluated based on 43 health indicators classified according to the international classification of diseases (ICD, 10th revision), including mainly those indicators characterizing mortality on cardiovascular and oncological diseases. In these areas the health status of population living in municipalities within creased PTE contents (As, Pb, Zn, Cu, Cd, Hg and Sb) was compared with that in advacent municipalities show in glow PTE contents. A total of 138 contaminated and 155 non-contaminated municipalities of similar socioeconomic, natural and geochemical-geological character were compared. PTE contents in soils of polluted municipalities reported considerably increased levels between 2 to 10 times higher in contrast to non-contaminated municipalities. On the other hand, PTE contents in groundwater were almost identical both in contaminated as well as non-contaminated areas and in majority of cases were below limit standard values for drinking water.
Based on the assessment of the health status of population (using 43 health indicators), no significant difference in the health status of population in contaminated and non-contaminated municipalities has been reported.

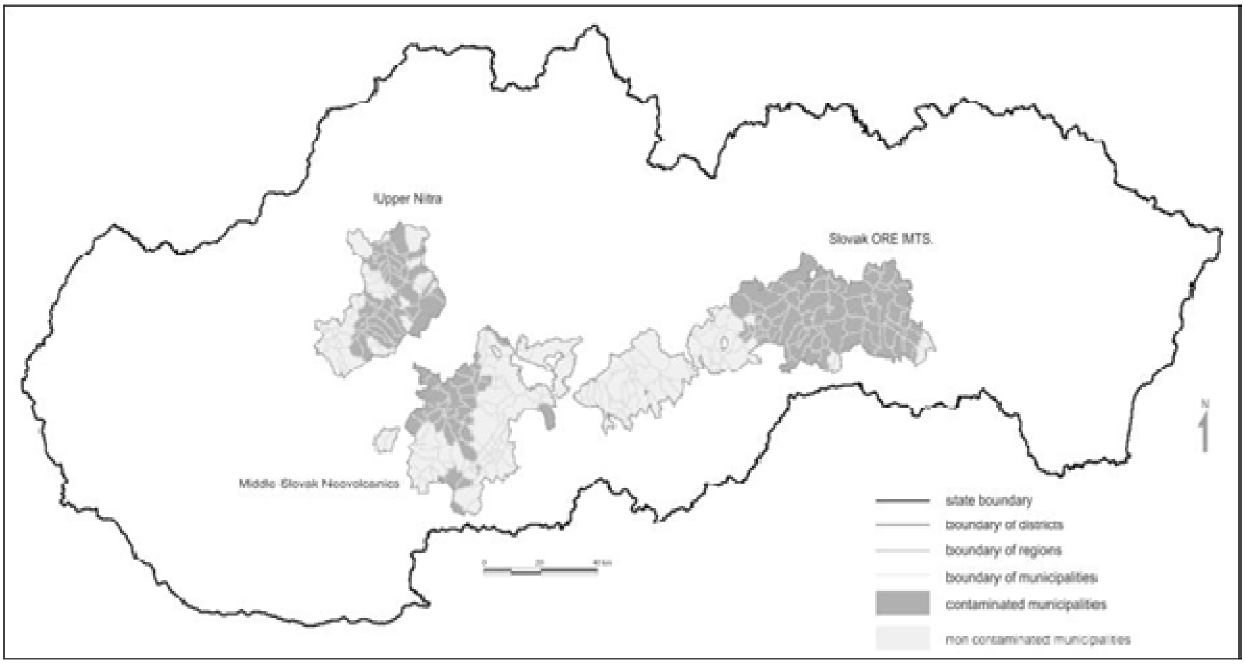

Fig. 1. Contaminated and non-contaminated areas of the Slovak Republic

ACKNOWLEDGEMENTS

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COMPREHENSIVE FACTS FROM THE GEOLOGICAL SURVEY OF THE CONTAMINATED SITE – VRAKUŇA CHEMICAL LANDFILL IN THE CAPITAL CITY BRATISLAVA

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KEYWORDS
Contaminated site, chemical landfill, pesticides, geological survey, pollution

ABSTRACT

The present article sumarizes results of a detailed geological exploration of the environment of the site Vrakuňa - skládka CHZJD. The survey was conducted within the framework of the MŽP SR's geological task entitled "Survey of contaminated sites on chosen sites of the Slovak republic ", part Survey of the environmental burdens on the Bratislava region site: Vrakunská cesta – CHZJD landfill". Landfill from Chemické Závody Juraja Dimitrova (CHZJD) was created in the period 1966 – 1979 by partly filling the waste channel and runway of Mlynské rameno of the Malý Dunaj with chemical waste originating from CHZJD and with supposedly inert material at a thickness of about 2 - 6 meters. The area of the landfill is approximately 46 500 m^2, the volume of the landfill material was set at 120 950 m^3 and the volume of the made ground above the waste at 156 430 m^3.
An execution of bottleneck probes in order to measure atmogeochemical parameters was carried out in the first phase of the field works. Measurements were performed with an ECOPROBE device. Probes reached depth approximately 2 – 2,5 m. The second phase subsequently took place in order to implement 25 pieces of unsupported exploration boreholes to the depth 8 m under the surface. Soil samples for determination of pre-selected contaminants were taken from unsupported boreholes. Geophysical measurements were conducted before and during the drilling works. Geophysical works mapped both possible area distribution of the waste as well as its depth interval. Total of 2 230 m of profiles were carried out. Geoelectric methods dipole electromagnetic profiling and electrical resistivity tomography were chosen from the available methods.
In the third stage 10 hydrogeological monitoring boreholes, completed in the impermeable clay bedrock, were constructed. Groundwater samples from wells in the town district Vrakuňa, as well as boreholes and wells in the possible outreach of the contamination, which included several boreholes and wells in the disctrict Podunajské Biskupice and municipality of Most pri Bratislave, were sampled in this phase of the works. Soil and groundwater samples were taken from three depth levels.

Considering EOCl analysis, most samples slightly exceeded the criteria but several cases showed concentrations above 2000 mg/kg. BTEX group exceeded limits for all substances, from which toulene reached most significant concentrations (5 390 mg/kg in the sample PVSV-4). When determining BTEX compounds, it is necessary to take into account the fact, that volatile substances are measured. Therefore it is necessary to bear in mind some degree of uncertainty, which enters the entire process of sampling. Halogenated organic compounds are expanded mainly in the soil air or in a dissolved phase in the groundwater. Among pesticides the highest concetrations were found with hexachlorobenzene (HCB) and hexachlorocyclohexane isomers (HCH).
A significant pollution of alpha HCH and its other isomers was discovered in the top layer of the landfill (0 – 3 m), which was supposed to consist of an inert material. High concentrations of PCBs (371 mg/kg), or Total Petroleum Hydrocarbons (47 300 mg / kg) in a cover layer raise questions about inertness of the material. High levels of petroleum hydrocarbons were found mainly in the area above the groundwater level and therefore there is no significant leaching to the groundwater. Among heavy metals, arsenic was dominant. The IT criteria were exceeded in about half of the samples with peak at 183-fold overrun.

In the groundwater all substances from the BTEX group significantly exceeded limits. Benzene appers to be most critical, whose limit has been exceeded more than 80 times. Plenty of chlorobenzenes from the group of halogenated volatile hydrocarbons exceeded limits (230-fold overrun of the IT criteria). These substances are used in numerous chemical, from which we mention pesticides and herbicides in particular. Isomers of HCH were the most significant pesticides found in the groundwater. They could originate as a by-product of lindane, which was produced in the former factory CHZJD. The most polluted samples contained concentrations of several hundred µg/l of alpha HCH, what represents more than 1 000-fold overrun of the IT criteria.

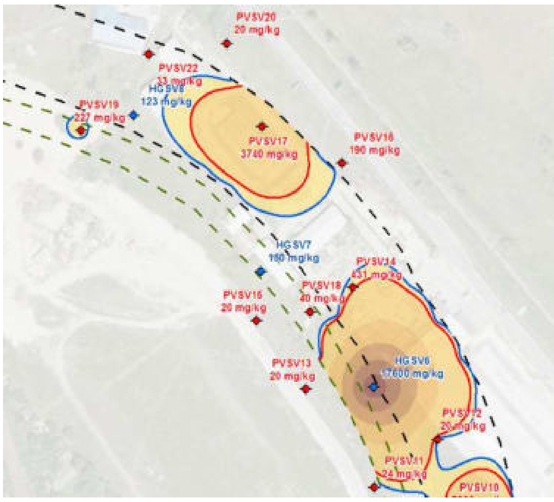

Fig. 1. Soil contamination with C10 - C40 fraction in the middle part of the landfill in the level 0 – 3 m bellow surface

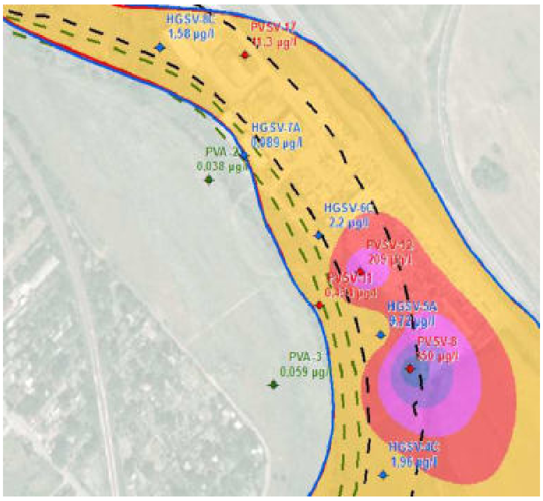

Fig. 2. Groundwater contamination with alpha HCH

More than 20 herbicides exceeded IT criteria. Some of them, such as chloridazon and prometryn exceeded the criteria in most of the samples including samples distant few kilometers from the source of pollution. While limits permit concentrations lesser than 1 µg/l, concentration in some samples reached values in units of mg/l. Selected herbicides together with HCHs belong to primary contaminants of the site.

The survey results confirmed a widespread contamination of soil gas, rock environment and groundwater with wide range of contaminants. Landfill area is highly polluted and is the source of groundwater pollution, which spread contamination in the groundwater flow direction.

The top layer of soil was supposed to be composed of an inert material but analysis showed elevated levels of a number of contaminants in this layer. The contamination has been demonstrated in all layers of the landfill body. A large number of substances exceeded ID and IT criteria. Among groups that reached the highest exceedance of criteria and also covered large area belong pesticides, herbicides and petroleum hydrocarbons.

Analyzes showed almost same contaminants in the soil and groundwater samples. While concentrations of petroleum hydrocarbons and arsenic in the groundwater are not as significant as in soils, concentrations of pesticides and herbicides are much higher, when compared to criteria. Most of the pollution is spread in the vicinity of the landfill, although several substances (eg. chloridazon or prometryn) spread over longer distances and reach into town districts of Vrakuňa, Podunajské Biskupice and even to municipality Most pri Bratislave.

A risk assessment makes clear that reviewed area of CHZJD landfill needs remediation as the site represents a serious environmental and health risks. A feasibility study identified variant of an active remediation to achieve the desired remediation limits as the most appropriate remediation conceptual variant.

ACKNOWLEDGMENT

We would like to thank multiple subcontractors for their part on the project. The project " Survey of contaminated sites on chosen sites of the Slovak republic" with ITMS code NFP24140111463 was conducted by Operational Programme Životné prostredie, Priority axis 4 - Waste Management, 4.1 Waste Management.

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PILOT TEST VERIFICATION TECHNOLOGY OF PERMEABLE REACTIVE BARRIERS FOR REMEDIATION OF ACIDIC GROUNDWATER

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KEYWORDS
caustic calcined magnesia (CCM), magnesite, wood chips/ wood shavings, reactive barier, heavy metals

ABSTRACT

The project titled "Authentication using the technology of permeable reactive barrier (PRB) for the remediation of acidic groundwater contaminated with heavy metals" is dealt with issues of permeable reactive barriers as one of the possible economical alternatives to costly remedial interventions. As already many times in the past confirmed, technologies and processes designed in the laboratory are sometimes difficult to apply in real terms. The project aims to transfer the laboratory conditions in a pilot plant scale, and verify the effectiveness of specially modified sorbent material technology simulating a permeable reactive barrier. To compare the effectiveness of the technology it was carried out several rounds of efficiency of technology both in laboratory and pilot scale.

Laboratory tests were performed in the laboratory of the Institute of Metallurgy, Faculty of Metallurgy, Technical University of Kosice, which is the principal investigator of the project. Laboratory tests aimed to find the most appropriate reaction carrier material and the material that would be capable of removing heavy metals from contaminated groundwater. After several attempts was the most suitable material used CCM (caustic calcined magnesia) with the carrier which are wood shavings measuring approximately 1.5 x 3 cm. The mixture was then tested to determine the best ratio to remove as much of the pollution from the used groundwater.

Fig.1. Laboratory equipment

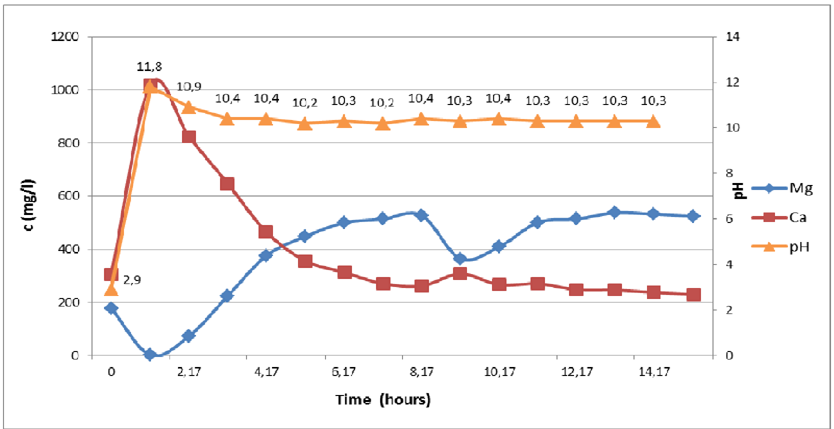

Fig.2. The dependence of the concentration of Mg^{2+} and Ca^{2+} cations and pH of the water at the outlet of the column from the time of the experiment (Kyslytsyna, 2016)

Great influence on the course of the clotting reaction has pH. During the experiment the observed changes in the pH and the concentration dependence of Mg^{2+} and Ca^{2+}. Caustic calcined magnesia (CCM) which was used had a high proportion of CaO. Therefore, during the first hours of the experiment, the reaction part in the precipitation of calcium oxide CaO, which increased the pH at 12. After exhaustion of entered CaO ,MgO reduced the pH to values of about 10, and remained constant. It was subsequently realized several tests with different variations of flow and retention time (Kyslytsyna, 2016).

Proven technology at selected sites preceded by a detailed survey of the site in terms of finding relevant documents necessary to run the pilot plant. Location was examined in detail in terms of the occurrence of surface contaminants and their quantification in space. The geophysical work were also used during executed surveys. These works helps to find the depth of impermeable bedrock what is necessary for the implementation of the draft of semi-permeable barrier (PRB). Part of field measurements were also hydrodynamic testing and measuring of physical-chemical parameters of groundwater pollution. To simulate the impact of realized PRB on the surrounding environment and particularly groundwater flow model was constructed. The model simulated the real state before pilot test and the scenario after the test of PRB.

Incorporated into the model were a number of variants in order to assess the economics of the whole implementation (compared to a model that takes account classical drawing at the limitation of the pollution in enclosed space). Pilot site has a very acidic environment of groundwater up to 1.5 - 3, wherein the water contains concentrations of heavy metals which exceed the limits laid down in Directive of Ministry of Environment (Directive of MŽP 2015). The samples from the technology were taken on a daily basis and there were also regularly measured physicochemical parameters of groundwater. As we can see the real situation shows more reactive material in total, which is closer to the real conditions of application of technology in the environment can cause changes in the properties of the behavior semi-permeable reactive barriers. Under real application conditions envisages the creation of preferential pathways of groundwater flow, which may adversely affect the efficiency of reaction barriers. This assumption appears to be an important factor for a successful and economically viable operation of a semi-permeable reactive barriers.

Fig.3. Technological equipment for a pilot line

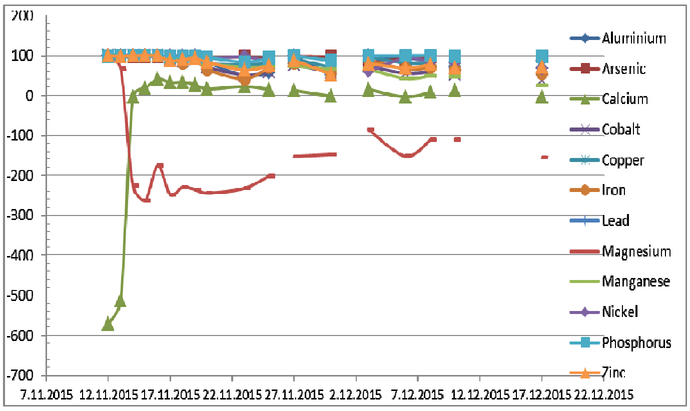

Fig.4. Removal efficiency for individual contaminants during the test

During the 7 day duration of the pilot plant testing to achieve virtually complete removal of the monitored contaminants - maximum efficiency values reached 98 to 100%. The next stage of the experiment there was a gradual decline in force of the aluminum (100% at 14.11 to 88% at 17.12.), Arsenic (from 98% to 97%), cobalt (from 100% to 37%), copper (from 98 % to 84%), iron (from 100% to 55%), manganese (from 100% to 25%), nickel (from 100% to 67%) and zinc (from 100% to 72%). Reported results are the basis for inputs for a pilot plant test. The results during the pilot plant test will be helpful for optimization flow of water in the technology.

Investigated combination of reaction material and the carrier appears to be an optimal solution also for practical application in practice, and will need to set all the technology to take account of the specific circumstances at a given location, which can achieve the status of universal application of technology for use in the PRB and on other sites where the dominant form of pollution, heavy metals and pH of the water is characterized by acidic conditions.

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ACHIEVEMENT OF MAPS OF SOIL VULNERABILITY FOR CONTAMINATION WITH HEAVY METALS USING STATISTICAL METHODS FOR CLUJ COUNTY (ROMANIA)

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KEYWORDS

Correlation analysis, heavy metals mobility, maps of vulnerability, regression analysis, Regression-Kriging method, soil contamination,

ABSTRACT

Population growth and industrial development have led to an intensification of the phenomenon of soil pollution with heavy metals. In the action to prevent and combat the consequences of this phenomenon is very important the knowledge of those special characteristics of soil that decisively influence the mobility of these metals in soils. Statistical processing of information, contained in available databases, can be particularly useful in developing maps of soil vulnerability to contamination with heavy metals. Having a such database at national level (Dumitru et al., 2000), containing 942 sites where was measured, at the same time, concentrations of eight heavy metals: Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn as well as the main physical-chemical characteristics of soil: clay content, pH and organic matter content, the authors presents, in this paper, the way in which were executed the maps of vulnerability for contamination with heavy metals for Cluj county (Romania). For these maps were used, successively, correlation analysis and non-linear regression analysis (for creating mathematical models) and I.D.W. method, respectively the Regression-Kriging method (for drawing the maps).

By using the contents of heavy metals and also the values of physico-chemical characteristics of all 942 sites, in a first step (Rogozan et al., 2013), were determined (by nonlinear regression) the mathematical models linking the heavy metals mobility by soil characteristics:

$\mathbf{Cd} = 2.6518 - 0.0708\mathbf{Cl} - 0.4795\mathbf{pH} + 0.1386\mathbf{MO} + 0.0087\mathbf{Cl{\cdot}pH} + 0.0037\mathbf{A{\cdot}MO} - 0.0444\mathbf{pH{\cdot}MO} + 0.0005\mathbf{Cl}^2 + +0.0329\mathbf{pH}^2 + 0.0161\mathbf{MO}^2$

$\mathbf{Co} = -21.2361 - 0.3105\mathbf{Cl} + 11.549\mathbf{pH} + 0.0363\mathbf{Cl{\cdot}pH} + 0.0048\mathbf{Cl}^2 - 0.9024\mathbf{pH}^2$

$\mathbf{Cr} = 103.753 - 0.3441\mathbf{Cl} - 22.418\mathbf{pH} + 0.1436\mathbf{Cl{\cdot}pH} - 0.0032\mathbf{Cl}^2 + 1.6567\mathbf{pH}^2$

$\mathbf{Cu} = -16.882 - 0.2621\mathbf{Cl} + 9.599\mathbf{pH} + 0.0365\mathbf{Cl{\cdot}pH} + 0.005\mathbf{Cl}^2 - 0.6759\mathbf{pH}^2$

$\mathbf{Mn} = - 357.38 + 4.2143\mathbf{Cl} + 231.92\mathbf{pH} + 1.3221\mathbf{Cl{\cdot}pH} - 0.149\mathbf{Cl}^2 - 20.647\mathbf{pH}^2$

$\mathbf{Ni} = -23.5132 - 0.9953\mathbf{Cl} + 15.649\mathbf{pH} + 0.2457\mathbf{Cl{\cdot}pH} - 0.0007\mathbf{Cl}^2 - 1.4947\mathbf{pH}^2$

$\mathbf{Pb} = 32.072 + 0.541\mathbf{pH} - 0.1639\mathbf{pH}^2$

$\mathbf{Zn} = 44.359 + 0.5937\mathbf{Cl}$

In these statistical models "**Cl**" variable represent clay content [%], "**pH**" variable – soil pH and "**MO**" variable – organic matter content [%]. The values for **Cd**, **Co**, **Cr**, **Cu**, **Mn**, **Ni**, **Pb** and **Zn** concentrations will be obtained in [mg/kg].

In the second step, using the I.D.W. method, for Cluj county were developed the maps for clay content, pH and organic matter (Rogozan and Micle, 2013). Built into the 54 sites, covering the whole area of the county, these three maps were used then, as predictors, in the Regression-Kriging method.

In this last stage Regression-Kriging method was used to generate vulnerability maps of soil contamination with heavy metals. The equations of these maps were derived from mathematical models above where, instead of punctual values for Cl, pH and MO, were introduced the interpolation equations of maps for the three physico-chemical characteristics at Cluj county level. The overall shape of these equations is:

$$\mathbf{Met}(x,y) = b_0 + b_1\mathbf{Z}_{\mathbf{Cl}}(x,y) + b_2\mathbf{Z}_{\mathbf{pH}}(x,y) + b_3\mathbf{Z}_{\mathbf{MO}}(x,y) + b_{12}\mathbf{Z}_{\mathbf{Cl}}(x,y)\mathbf{Z}_{\mathbf{pH}}(x,y) + b_{13}\mathbf{Z}_{\mathbf{Cl}}(x,y)\mathbf{Z}_{\mathbf{MO}}(x,y) + b_{23}\mathbf{Z}_{\mathbf{pH}}(x,y)\mathbf{Z}_{\mathbf{MO}}(x,y) + b_{11}\mathbf{Z}_{\mathbf{Cl}}(x,y)^2 + b_{22}\mathbf{Z}_{\mathbf{pH}}(x,y)^2 + b_{33}\mathbf{Z}_{\mathbf{MO}}(x,y)^2$$

where **Met**(x,y) is the heavy metal content retained in soil at the point of coordinates x,y and $\mathbf{Z}_{\mathbf{Cl}}(x,y)$, $\mathbf{Z}_{\mathbf{pH}}(x,y)$, $\mathbf{Z}_{\mathbf{MO}}(x,y)$ are the values of all three physico-chemical characteristics (computed using the predictors maps) in the same point. For two of these heavy metals (Cr, and Pb) these maps of vulnerability are shown in Figures 1 and 2.

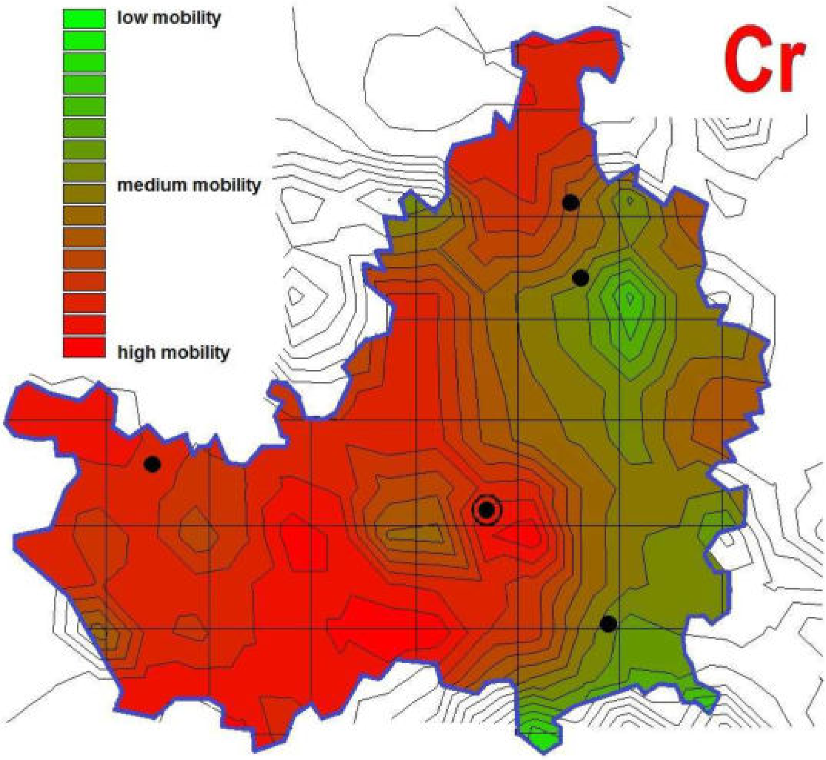

Fig. 1. Soil vulnerability at Chrome contamination for Cluj county.

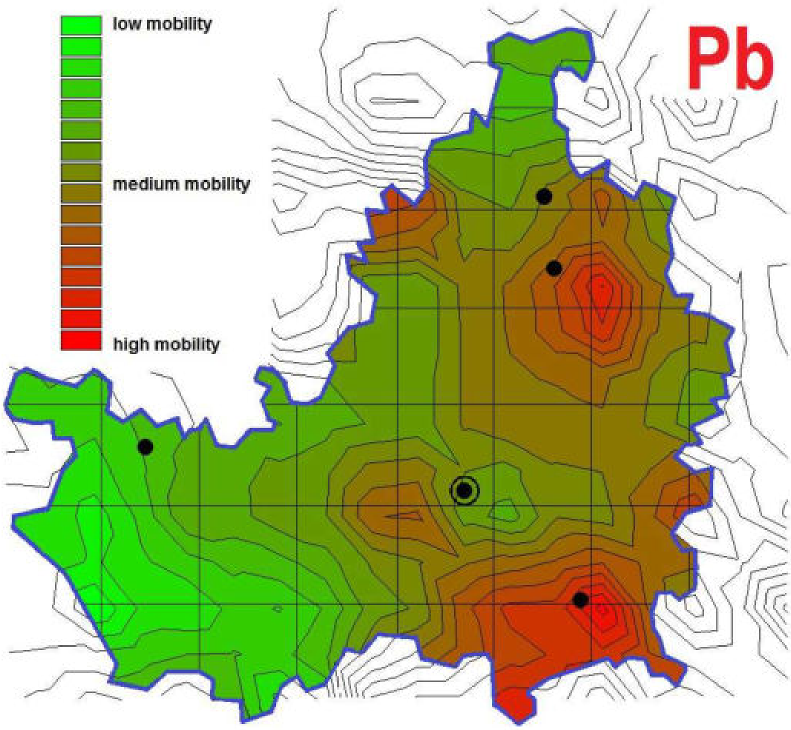

Fig. 2. Soil vulnerability at Lead contamination for Cluj county.

The red areas indicate a high risk of contamination, because they have a poor retention capacity for the pollutant, while the green areas have a good binding capacity preventing contamination expansion.

ACKNOWLEDGEMENTS

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USE OF MULTIPLE BIOMARKERS TO EVALUATE PLANT SPECIES SUITABILITY TO MANAGE CONTAMINATED AREAS

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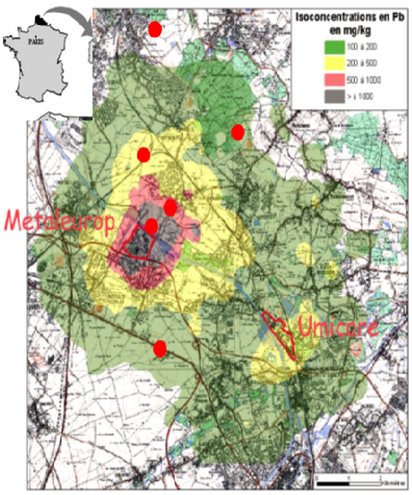
KEYWORDS
Biomarker, heavy metals, metal accumulation, oxidative stress, plant stress, photosynthesis, phytostabilisation, phytomanagement, pollution

ABSTRACT

The use of plants and associated microorganisms has been increasely consider as a sustainable and cost-effective option to manage contaminated areas. Phytomanagement is mainly based on the ability of plants to uptake (phytoextraction), stabilize (phytostabilization) or degrade (phytodegration/rhizodegradation) pollutants. It aims at reducing human and environmental risks while stimulating ecological restoration and restoring landscape.
The selection of plant species or cultivars to manage contaminated sites is mainly based on their ability to stimulate organic pollutant degradation and/or to reduce pollutants mobility or increase pollutant uptake. However, despite phytoremediation approaches are long-term techniques, only limited studies have focused on plant long-term ability to survive on contaminated areas. Most of studies are short-term experiments (few weeks/months) lead into greenhouses. Moreover, plant health is superficially evaluated using few macroscopic markers (germination, plant growth, number of leaves…) or biomarkers at molecular scale (antioxidant enzymes, photosynthetic pigments…). This lack of concern about plant health explains the limited success of several *in situ* phytomanagement studies. Thus, there is a need to develop alternative methods to evaluate plant long-term ability to survive on contaminated areas.
Here, we investigated sub-lethal effects of contaminated soil exposure on three plant species described as good candidates for phytomanagement of contaminated areas: ryegrass (*Lolium perenne*), clover (*Trifolium repens*) and miscanthus (*Miscanthus x giganteus*). Plants were grown during 8 weeks into pots containing a range of contaminated soils (Fig. 1) collected around the former lead smelter Metaleurop Nord (Northern France).



Soil	[Pb] mg.kg^{-1}	[Cd] mg.kg^{-1}	[Zn] mg.kg^{-1}	pH$_{water}$
Control	32	0.6	76	6.9
2B	101	1.9	150	6.6
17B	240	4.9	307	7.5
28B	451	8.8	587	7.8
35B	777	14.9	1000	8
33B	1079	19.2	1371	7.9

Fig. 1. lead isoconcentration curves (left) around the former lead smelter Metaleurop Nord (contaminated area ~ 120 km^2), and soil heavy metal concentrations in the studied soils (right).

We analyzed metal uptake into roots and translocation to above ground parts. Meanwhile we also monitored several biomarkers (oxidative stress, lipid peroxidation, photosynthetic pigments, DNA degradation) to evaluate plant health.

Our results clearly demonstrated the ability of the 3 studied plants to stabilize heavy metals into their root system (Fig. 2). The low translocation to above ground parts supports their interest to be used to phytomanage contaminated sites.

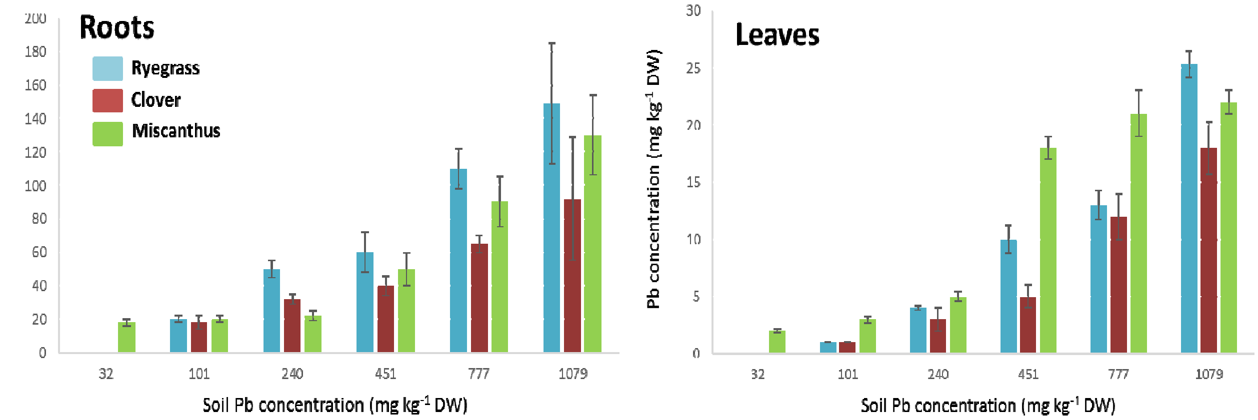


Fig. 2. Lead concentrations into plant roots and leaves

However, investigating heavy metal effects on plant health, our results show different metal tolerances among these plants. Despite its potential to stabilize pollutants in soils, ryegrass plants exhibited high level of oxidative stress, lipid degradation and DNA stand breaks (Fig. 3).

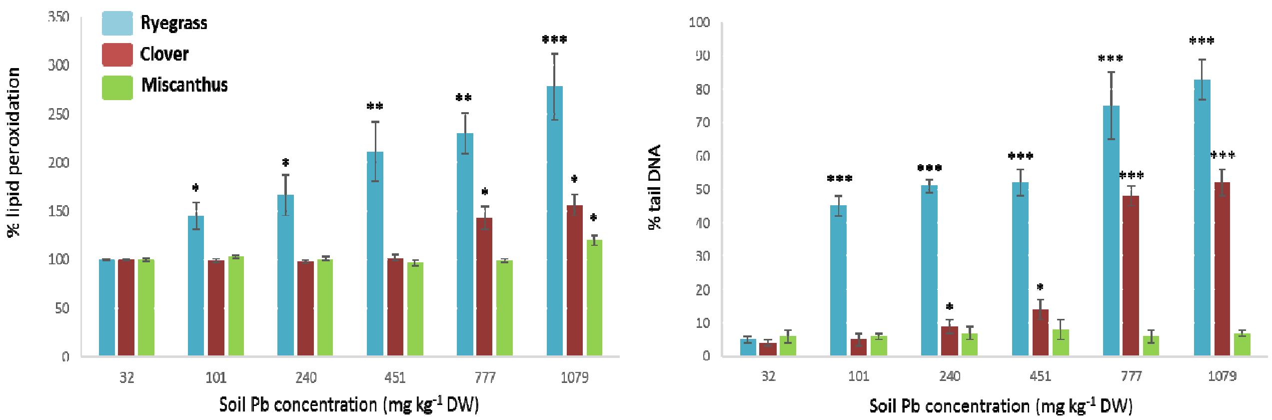


Fig. 3. Effect of heavy metals on lipid peroxidation evaluated by measuring MDA formation (left) and DNA degradation evaluated by measuring % of DNA strand breaks by comet assay (right).

These results challenge the suitability of this plant for a long-term management of contaminated soils. In the other hands, miscanthus plants showed little effects of metals, event at extremely high concentrations. This confirm this plant as good candidate for phytomanagement. These greenhouse experiments were confirmed by *in situ* long-term experiments (6 years), highlighting the interest of using biomarkers to select plants for contaminated area management.

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STUDY OF NAPROXEN AND DICLOFENAC REMOVAL IN MODEL AND REAL WATER SAMPLES BY PHOTOCATALYTIC PROCESSES

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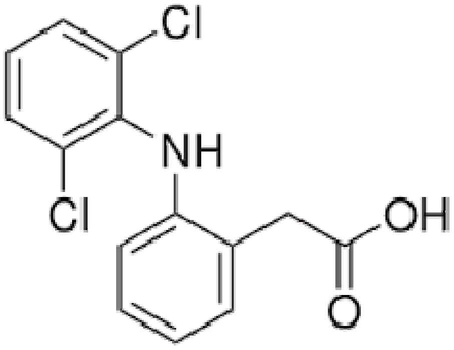
KEYWORDS
Pharmaceuticals, diclofenac, naproxen, heterogeneous photocatalysis

ABSTRACT

Pharmaceuticals belong to chemical substances that can be currently increasingly detected in environmental matrices. Their concentrations vary in the order of ng/L to µg/L and at this concentration they can chronically affect non-target organisms because of their strong biological effect on living systems. Diclofenac and naproxen were chosen due to its widespread consuption, relatively high toxicity and detection in waterways. These pharmaceuticals were from model water samples removed by heterogeneous photocatalysis in 4L batch reactor. As a source of UV light a UV-LED system Luminus was used with a peak emission of 365 nm. As a catalyst TiO2 (AV-01, Precheza, CR) was used at a concentration 0.5 g/L. The influence of hydrogen peroxide and pH adjustment on mineralization process is evaluated. Also characteristics of real surface water from river Labe and possibilities of pharmaceutical removal in this matrix are discussed.

Naproxen [(S) 6-methoxy-α-methyl-2-naphtalene acetic acid] and diclofenac (2-(2-(2,6-dichlorophenylamino) phenyl)acetic acid are members of nonsteroidal anti-inflammatory drugs (NSAIDs). These two pharmaceuticals are often detected in surveyed water abroad, but recently in Czech Republic too. Chemical structures of these pharmaceuticals are described in Fig 1.

a)



b)

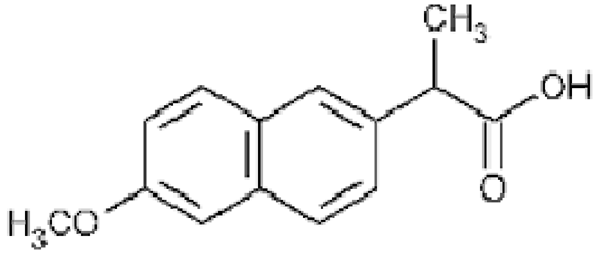


Fig. 1. Chemical structures of diclofenac (a) and naproxen (b).

To better know the oxidation power of the method, pharmaceuticals were removed from model samples. Just by UV photolysis was removed only 17 % and 25 % of each pharmaceutical. Coupling UV photolysis with the effect of catalyst, the photocatalytic degradation started. The removal rate of heterogeneous photocatalysis was 99 % and 82 %. During photocatalysis with peroxide addition was removed 99 % of diclofenac and 86 % of naproxen. Best results were achieved during heterogeneous photocatalysis in acidic pH (100% and 92% removal).

In Tab. 1 are shown parameters of waste water. After 1 hour of heterogeneous photocatalysis, these parameters decreased. On the other hand non selective manner of hydroxyl radicals was confirmed. After photocatalysis in wastewater, only up to 20 % of the drugs were removed. After addition of H_2O_2 significantly improve the degradation of the pharmaceuticals in these waters. It was removed 76 % of diclofenac and 67 % of naproxen. Next experiments will be focused on removal of pharmaceuticals in acidic ph in combination with the effect of hydrogen peroxide.

Tab. 1. Parameters of WWTP before and after heterogeneous photocatalysis

Parameter	Before photocatalysis	After photocatalysis
pH	7.7	7.6
COD_{Cr} (mg/L)	351	250
$N\text{-}NO_3^-$ (mg/L)	1.6	0.75
$N\text{-}NO_2^-$ (mg/L)	0	0
$P\text{-}PO_4^{3-}$ (mg/L)	1.7	1.4
A_{254} (ZF)	122.9	76.8
CFU	3.24x106	2.24x105

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EXPERIENCES FROM PROFESSIONAL GEOLOGICAL SUPERVISION ON REMEDIATION OF SITE QUARRY SRDCE

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KEYWORDS
Gudron, soil, groundwater, excavation, remediation, contaminants, professional geological supervision, quarry

INTRODUCTION

On the site quarry Srdce has been made one of the first professional geological supervision (PGS) as part of remediation program for the contaminated sites in Slovakia. PGS was realized according to the requirements of the Act 569/2007 Z.z. on geological Works.
The remediation itself consisted of removing contaminated material – "gudron" (sludge, organic acid petroleum residual products) from environment and revitalized the quarry. The purpose of remediation activities was eliminating human and environmental risks resulting from possible exposures of contaminants by spreading them to the ambient environment (Fig. 1).

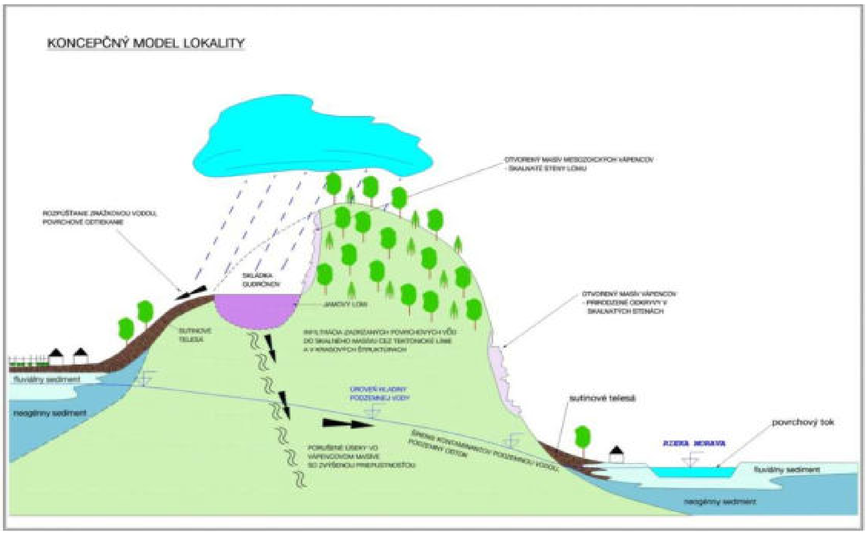

Fig. 1. Conceptual model of locality.

ACTIVITIES OFPGS

One of main task for PGS activities was to ensure that remedial work has been carried out in good quality, effective, in accordance with the acceptation of the project, according to the approved schedule and the approved budget. At the same time it was necessary overseeing the implementation of remediation for compliance with applicable laws, regulations and standards.
Individual activities PGS were designed so as to meet the objective of geological problems – completely removing storage of gudron from the quarry. Methodology for PGS activities considered all results from previous geological survey and risk assessment with respect to physical-chemical properties of hazardous waste deposited in a quarry, difficulties of terrain and the condition of the quarry.
The key activities of PGS:
- Monitoring the effectiveness of the funds spent in relation to the desired outcome of the project,
- Evaluating of remediation work development,
- Providing of feedback for timely detection of problems,
- Preparation of proposals for corrective action.

Additional activities of PGS:
- Control over implementation for required range of remediation activities set upped by the project,
- Verification of documentation and data sets,

- Verifying of achieved remediation limits,
- Control of the implementation of remediation for compliance with applicable laws, regulations and standards (in particular Act no. 569/2007Coll., and Decree no. 51/2008 Coll.).

Activities of PGS were also oriented to check the effectiveness and accuracy of the remediation by field measurements, sampling and laboratory analyzes throughout the period of remediation (Fig. 2.1 – Fig. 2.3).

Fig. 2.1. Sampling of soil from the contact zone from SW part of quarry

Fig. 2.2. Sampling of groundwater from the borehole DS-1

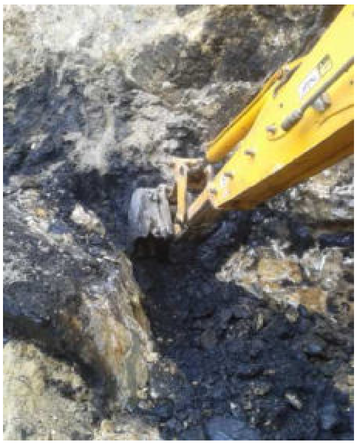

Fig. 2.3. Finishing of cleaning works from the crevasses of quarry

RESULTS AND CONCLUSION

The locality was remediated in accordance with the approved project. The total excavating amount of hazardous waste (acid tars and contaminated soil) was 18 400 m^3 of acid tars and 14 150 m^3 of contaminated soils including cover layers. In handling hazardous waste, it was preceded in accordance with applicable legal regulations.
To demonstrate fulfilling of remediation limits relatively dense network of sampling places was necessary to applied. Despite the highly heterogeneous nature of soil on the bottom of quarry it has been shown that the residual soil material at the quarry bottom is clean.Control of groundwater sampling was considerably limited. On most of objects the groundwater was not reached. Sampling was possible realized only in one monitoring well and then also in older objects situated further away from landfill. Due to this situation it was use the opportunity of additional occasional sampling of surface water, which originated from rainfall on the surface of gudron.
A challenge in the implementation of remediation works was removing of waste material from the quarry walls and crevasses. For these purposes were applied various technics: excavator, hand treatment, hydraulic purification, and best-applied application of special air blasting with addition of sand as an abrasive.The final clean up works were controlling primarily sensorially in-situ. It was observed the presence gudron on the surface of each key sector: the quarry walls, surface of the quarry bottom, driveway, handling areas.Within backfilling the quarry it was necessary to record the "purity" of the imported soil material for recultivation of quarry to prevent unwanted contamination. The frequency and extent of sampling adapted to the operational state of filling the quarry with clean soil: weather, days off, the availability of soil, etc.
Sequence, management and coordination by the PGS in the course of all geological and remediation work at the site was carried out in collaboration with the contractor and customer (Ministry of Environment of SR). In addition to participation in control days, was the presence of PGS on the site depending also on the progress of remediation works. This part is very important to achieve remediation goals. It is necessary to participate on ongoing activities directly from beginning only that way is possible to ensure effective approach for remediation.

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INTEREST OF *MISCANTHUS* BIOCHARS TO DECREASE THE AVAILABILITY OF METALS IN AQUEOUS SOLUTIONS

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KEYWORDS
Biochar, *Miscanthus*, contaminated biomass, metals, aqueous solution, adsorption kinetics, desorption

ABSTRACT

Soil is an essential and non-renewable resource which can perform a high number of economic, social and environmental functions as biomass production, source of raw materials or protection of humans and environment (Blum, 2005). However, the soil functionality becomes increasingly compromised due to contaminations caused by human activities. For example, in 39 countries, the European Environmental Agency inventoried more than 2.5 million potentially contaminated sites, mostly polluted by metallic elements (34.8%) (EC-European Commission, 2001).
Some of remediation techniques to restore these soils (e.g. excavation) are considered inappropriate because they generate considerable disturbances, are expensive and economically unfeasible on a large scale (Fig. 1).

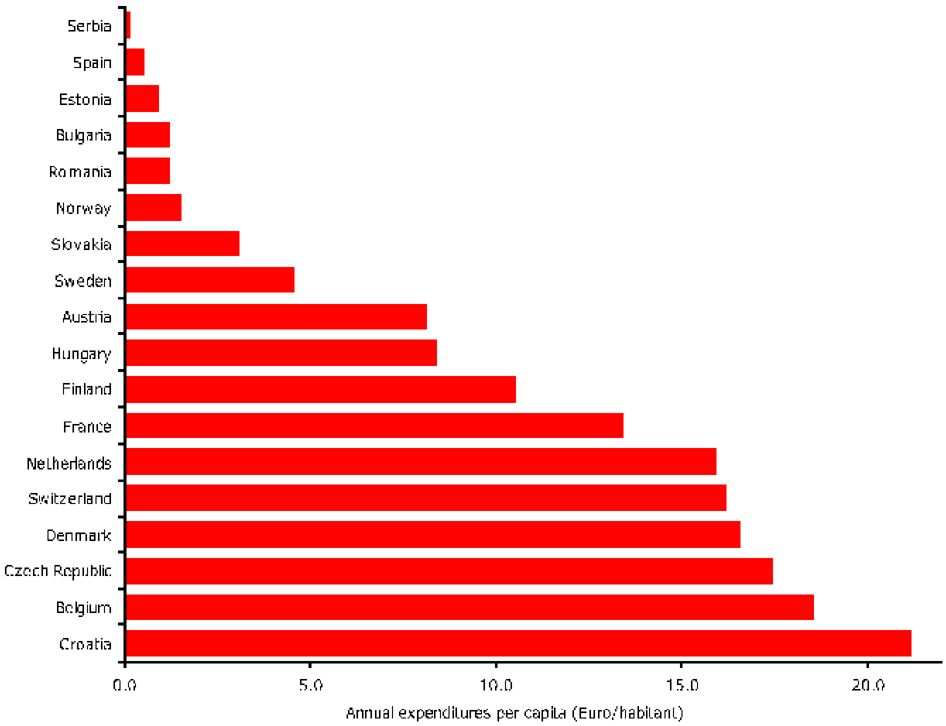

Fig. 1. Annual national expenditures for management of contaminated sites (EUR per habitant) (EEA, 2009).

For some years now, an *insitu* technique consisting in introducing amendment in contaminated soils has shown the ability to decrease the pollutant bioavailability (Beesley et al., 2011; Yu et al., 2009). Among the different amendments that can be used to remediate contaminated soils, the biochars seem promising. Biochars are defined as the carbon-rich products obtained by pyrolysis when biomass (e.g. wood or manure) is heated in a closed container with little or no available air (Lehmann and Joseph, 2009). Many studies demonstrated the ability of biochar to decrease the bioavailability of metallic elements in soils (Kim et al., 2014; Rodríguez-Vila et al., 2015). However, it has been shown that the production parameters of biochars can affect their characteristics and thus their effects on the physicochemical and biological characteristics of soils after their amendments(Janus

et al., 2015). An examination of the scientific literature revealed that the type of feedstock, the temperature, the heating rate and the gas flow of the pyrolysisare the major parameters influencing the biochar characteristics.
The goal of the present work consists in evaluating the metal sorption capacity of nine biochars in aqueous solutions. Eight biochar samples were produced by the French agricultural research organization CIRAD (France) from *Miscanthus x giganteus*, a non-wood rhizomatous perennial grass, grown on an agricultural land contaminated by metals located near a former lead smelter (Metaleurop Nord, France; Fig. 2). These biochars were produced according to different pyrolysis parameters (*i.e.* temperature: 400 and 600°C, heating rate: 5 and 10 °C min^{-1} and residence time: 45 and 90 min). In addition to these eight biochars, a biochar made from wood, already commercialized, was also used in this experiment. It was produced by the Carbonerie Ltd. (France) at a temperature of 400°C during 12h.

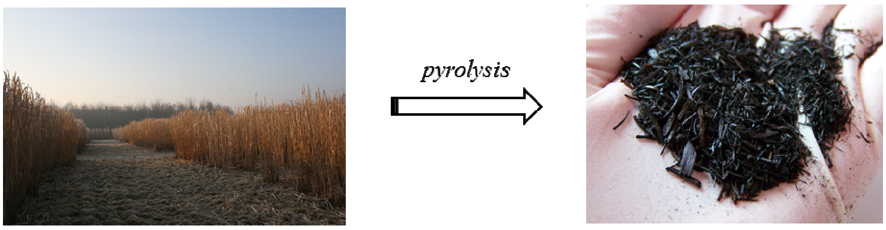

Fig. 2. Field of *Miscanthus x giganteus* and its conversion into biochar.

First part of the study consisted in measuring chemical and physical parameters of the biochars. Second part aimed at comparing the efficiency of these different biochars to decrease the availability of Cd, Pb, and Zn in spiked solutions when these metals werei) alone in the solution, ii) mixed together and iii) mixed together with eight polycyclic aromatic hydrocarbons(PAHs). For this purpose, the sorption pollutant efficiency by the biochars has been evaluated during 7 days in aqueous solutions then following by a 7 day desorption in order to evaluate the sorption durability of pollutants by the biochars.
The biochar characterization revealed that the biochars produced at the highest temperature presentthe highest ash and carbon contents, pH and specific surface areas.These parameters can strongly affect the sorption efficiency of biochars. After the sorption/desorption cycles, the results showed a high efficiency of *Miscanthus* biochars to sorb Cd, Pb and Zn, especially those produced at the highest temperature. When the metals were mixed with the eight PAHs, the biochars produced at the lowest temperature revealed lower sorption efficiency, notably for Zn, showing competition process between the contaminants for the sorption sites on biochars. The desorption study revealed lowest release for the biochars produced at the highest temperature. However, all the biochars presented low desorption, showing a strong sorption durability of pollutants.
To conclude, the first results obtained showed that i) the pyrolysis process highly impacts biochar characteristics, ii) the studied biochars show a high efficiency to sorb the metals in aqueous solutions.

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REVITALIZATION OF CHEMICAL DEGRADED SOILS USING PLANT FOLIAR NUTRITION

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KEYWORDS
Foliar fertilizer, soil fertility, cabbage, potato, corn

ABSTRACT

Multiannual improper application of fertilizers in the soil leads to strong changes in the solum. It causes disorders of the soil properties that reflect the reduction of productivity and soil fertility. Foliar nutrition represents an application of water soluble fertilizers directly through the plant leaf. Its effectiveness is estimated based on absorption and availability of components, reduction of phytotoxicity, deficit of nutrients, impact on physiological-biochemical processes of plants, as well as on the yield and quality of culture.
In order to examine the effect of foliar fertilization on the yield of potatoes, cabbage and corn, research was conducted in three variants for each culture. Variants in the experiment were: 1 – Control (untreated), 2 – Humustim and 3 – Ingrasamant Foliar.
It was found that in the variant with foliar fertilizer the yield is increased significantly compared to the control variant. The highest yields were achieved in potatoes (38.71 t/ha) and corn (10.41 t/ha) in the variant with application of ingrasamant foliar, while in cabbage (90.96 t/ha) with aplication of humustim.
In conditions of high soil fertility with nutrients, the application of ecological foliar fertilizer enables profitable yields. Thereby simultaneously maintain a clean environment and optimal and economically justified plant production.

INTRODUCTION

Successful agricultural production is based on "healthy" soil which by its biological activity and natural fertility can provide obtaining high quality products. The soil through its physical, chemical and microbiological properties provides conditions for growth and development of plants. In terms of plant nutrition, great importance has the knowledge of water, air, heat, biological and nutritional regime of the soil.
In agriculture man treats the soil as an environment for plants in which they grow, develop and give yields. We distinguish: soil productivity and fertility of the soil.
Soil productivity is closely related to soil fertility and implies the ability of the soil to deliver yields of a certain plant under certain climatic conditions and under certain farming practices.
Soil fertility means the ability of soil to continually secure the plants throughout their life at certain times, as well as give them food, water, air and other amenities at the same time. It is variable and changes under the influence on the constant changes taking place in the soil and on the surrounding environment. Profound changes in soil fertility can be carried by anthropogenisation.

MATERIAL AND METHOD OF OPERATION

Scientific research experiment is set in the area of the village Negorci, Gevgelija (Macedonia) on a surface which for years has been used for vegetable production intensively fertilized with mineral and organic fertilizers. The research included crop cabbage (Brassica oleracea L. var. Capitata), variety Sacato, potato (Solanum tuberosum), variety volumnia and corn (Zea mays), hybrid 444. The experiment is inserted and attached in generally accepted normatives and methods for setting field experiments according Filiposki (2004). Foliar application of fertilizers is carried out with 0.4% aqueous solution of fertilizers, using a dorsal nozzle every 10-20 days, three times during the vegetation. The first application of fertilizers is established at adequate leaf mass, i.e. the phase of two true leaves. While harvesting, crops measurement is performed on individual variations and repetitions.
The experiment involves the following variants:
1. Control (variant without application of agro-technical measure - fertilizing);
2. Variant with application of foliar fertilizer – Humustim;

3. Variant with application of foliar fertilizer – Ingrasamant foliar.

The fertilizer of the second variant, Humustim, is categorized in the group of organic fertilizers and is characterized by the following chemical properties: total organic matter = 58.63%, total dry matter = 12.38% humic acids = 20.40%, fulvic acids = 2.15%, N = 3.00%, P_2O_5 = 1.02%, K_2O= 7.92%, Ca= 3.70%, Mg= 1.03%. The chemical properties of the fertilizer are given in the manufacturer declaration.
The third variant is performed by application of the foliar fertilizer Ingrasamant foliar, from the group of organic and mineral fertilizers, and according to the manufacturer declaration, it is characterized by the following chemical properties: N= 0 g/l, P_2O_5 =130 g/l, K_2O =130 g/l, ME in chelated form, plant extracts 0.005 g/l.

Before the installation of the experiment average samples have been taken at a depth of 0-20 and 20-40 cm for determination of the chemical properties of soil and that determination included:

- Determining of soil solution pH-reaction (in H_2O and N KCl), content of organic carbon and humus, total nitrogen content, determined according to the Tjurin method, content of physiologically available forms of nitrogen, determined by Tjurin and Kononova method, content of physiologically available forms of phosphorus and potassium, determined according to the AL-method (Bogdanovič, 1966);
- Determining of carbonates, hydrolytic acidity and amount of base cations in absorbed carbonate-free soils according to the Kappen method and calculation of the cation absorption capacity and the degree of saturation of the soil with base cations (Mitrikeski and Mitkova, 2013).

RESULTS AND DISCUSSION

Tab. 1. Chemical properties of the soil

Depth in (cm)	pH		%			Available forms in mg/100 g soil			eq.mmol/100g			%
	H_2O	N KCl	$CaCO_3$	Humus	Total N	N	P_2O_5	K_2O	H^*	S^*	T^*	V^*
0-20	7.35	6.71	0.00	3.30	0.20	13.61	126.00	65.35	1.39	41.64	43.03	96.77
20-40	7.40	6.73	0.00	2.61	0.16	12.44	122.33	64.28	2.45	57.01	59.44	95.91
Average	**7.38**	**6.72**	**0.00**	**2.96**	**0.18**	**13.03**	**124.17**	**64.82**	**1.92**	**49.33**	**51.24**	**96.34**

From the obtained results interpreted in Table 1 it can be concluded that the soil is characterized by a neutral pH reaction and high humus. The soil is characterized by a high adsorption capacity (> 30 eq.mmol / 100g absolutely dry soil and a large saturation of the soil with basic ions (Ca and Mg over 90%).
The values obtained for the nutritional elements note immense imbalance of nutritional regime in the soil, i.e. imbalance of the content of physiologically available nutritional elements. The content of the three main macro-biogenic elements is relatively high, and the situation with the phosphorus is particularly alarming. In our case, at extremely high concentrations of nutritive elements in the soil, application of soil fertilizers would have a negative effect and would further deteriorate the current soil fertility, including negative influence over other components of the environment. Having in mind the ultimate goal in vegetative agricultural production (obtaining higher yields characterized by better quality), only application of foliar fertilizers and cultivation of cultures for which other soil properties would be primarily fitting would satisfy these needs while maintaining a clean environment (Petrov, 2014).

Tab. 2. Yield of cabbage, potato and maize expressed in t/ha in variants

Variant	**Yield cabbage t/ha**	**Yield potato t/ha**	**Yield corn t/ha**
1 Control	79.07	29.48	9.14
2 Humustim	90.96	37.19	9.66
3 Ingrasamant foliar	90.02	38.71	10.41

From the data presented in Table 2 it can be concluded that the application of foliar fertilizers in the three cultures has a positive impact in increasing yield, and thus the utilization of nutrients from the soil.
The highest yields were achieved in potatoes (38.71 t/ha) and maize (10.41 t/ha) with application of foliar ingrasamant, while cabbage (90.96 t/ha) using Humustim.

CONCLUSION

Based on the theoretical postulates and the research results it can be concluded that given the high content of nutrients in the soil, the application of soil fertilizers would have a negative effect on the growth and development of plants and more would have deteriorated the nutritional regime of soil.
Foliar application of fertilizers in terms of impaired nutrient regime has a positive impact on the yield of cabbage, potatoes and corn.

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ASSESSMENT OF MICROBIAL POTENTIAL IN BIOREMEDIATION OF CONTAMINATED TECHNOSOLS

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KEYWORDS
Contamination, potentially toxic elements, technosols, microbial remediation

ABSTRACT

The study deals with microbiological aspects of technosols and consequently with the use of autochthonous microbiota living in the environment to remove potentially toxic trace elements (PTTEs) from the soils. This work deals with two types of atypical soils (technosols) with different environmental burden. First locality - Zemianske Kostoľany - represents an interesting ecosystem, which was established more than 40 years ago. Long-term exposure and selection pressure of elevated concentrations of arsenic (a range of 93–634 ppm) induced the formation of the specific adapted autochthonous microorganisms. In these highly As contaminated soils affected by the presence of buried ashes from brown coal combustion, not only species identified for the first time in Slovakia, but also new strains of bacteria, that sequences have been deposited in GenBank database, were found. Despite the stimulation of autochthonous community by nutrient medium and augmentation by native species, As leachability was relatively low - on average 5.63 wt.%, 9.23 wt.% and 17.04 wt.% of the total As for inoculated *Pseudomonas chlororaphis* ZK-1, *Pseudomonas putida* ZK-5 and *Aspergillus niger*, respectively. The highest As leachability was achieved through biostimulation of autochthonous microbiota using liquid SAB medium (34.73 wt.% of total As content). Additionally, microbial activity was efficient in the biovolatilization of As from soils (~70 wt.% of the total As volatilized).

Second locality is abandoned Sb deposit Poproč, that soils from the surrounding mining area and wastes are enriched in a variety of PTTEs, mainly with As, Sb, Zn and Pb levels up to 1463 ppm, 5825 ppm, 1202 ppm and 424 ppm, respectively. The extractability of selected PTTEs was evaluated by single extraction with inorganic and organic extractants. The highest extractabilities were found when organic single-extraction techniques were applied. The average bioleaching efficiency of elements with liquid Sabouraud medium was: Zn (55.71 %) > As (40.74 %) > Sb (14.38 %) > Pb (10.01 %). The addition of glucose to the liquid Sabouraud medium increased the release of elements due to activation of heterotrophic microorganisms and sequence of leaching efficiency was: Zn (64.90 %) > As (50.66 %) > Sb (14.55 %) > Pb (8.5 %). The second type of biological treatment involved the use of the autochthonous microorganisms (AM), whose activity was combined with the inoculation of *C. metallidurans* or *C. oxalaticus* (allochthonous species). At the end of the experiments with *C. metallidurans* and *C. oxalaticus*, average As solubilization efficiencies were noted as 37.58 %, 41.33 % and Sb as 17.03 %, 26.24 %, respectively (Fig. 1).

It appears that bioremediation using microorganisms represents one of the possible ways of PTTEs removal from soils containing different anthropogenic materials with elevated concentrations of PTTEs.

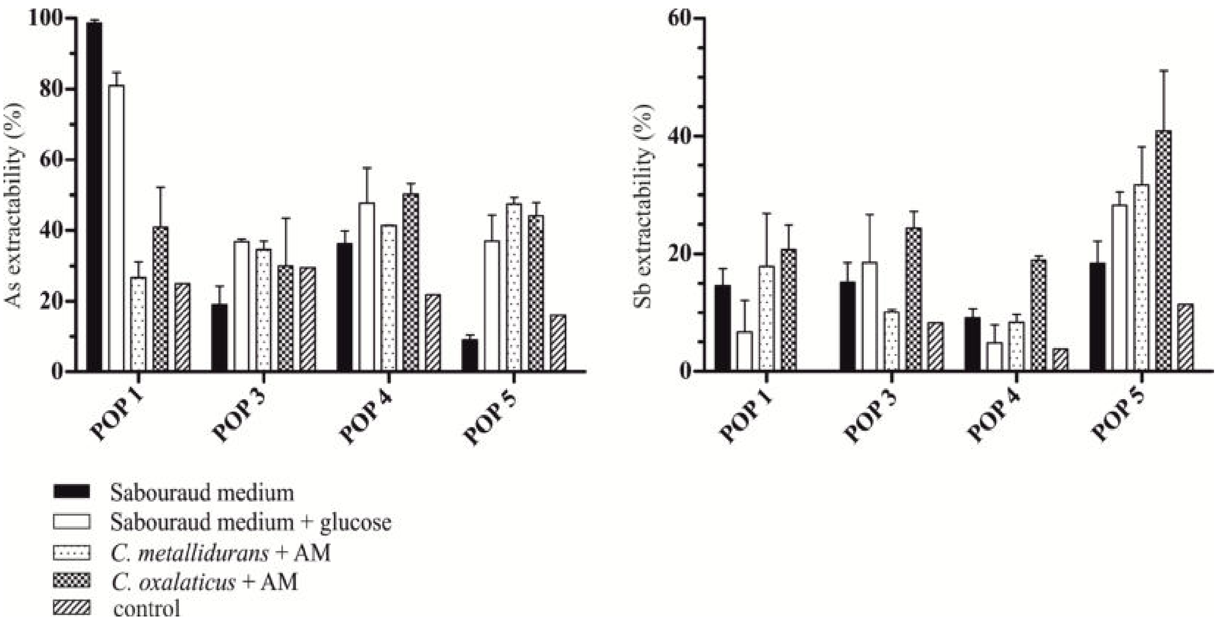

Fig. 1. Comparison of the final solubilization efficiencies (%) of As and Sb from solid samples in the bioleaching process using the different leaching conditions (mean values ± standard deviations).

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DETERMINATION OF THE SPECIFIC SURFACE OF THE MODIFIED FORMS OF ZEOLITE NAY WITH LACTIC, CITRIC AND HYDROCHLORIC ACID

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KEYWORDS
Zeolite NaY, dealumination, specific surface,Langmuir isotherm

ABSTRACT

Zeolite NaY with its structure corresponds to the natural zeolite foshazit. NaY zeolite has the following formula:
$Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O \rightarrow Na_{12}(AlO_2)_{12} \cdot (SiO_2)_{12} \cdot {}_{27}H_2O$
Its structure is strong and it is necessary to perform dealumination to be used as an adsorbent. In present examinations dealumination is performed, extracting Al structure from NaY zeolite, by using a solution of 0.2 mol/dm3 lactic, 0.2 mol/dm3 citric and 0.1 mol/dm^3 hydrochloric acid. Reaction time was 2 hours at room temperature. The obtained modified forms of zeolite are tested with a static gravimetric method. Adsorbtion isotherms are from Langmuir type. With linearization of isotherms the specific surface is determined according to the equation $S = a_m \cdot A_m \cdot 6.023 \cdot 10^3$ [m^2/kg $\cdot 10^3$]. The determined specific surface of the modified forms of zeolite ranges from 43.7819 to 70.3769 m^2/kg $\cdot$ 10^3 depending on the selected operating parameters of dealumination.
The obtained modified forms of NaY zeolite can be used for adsorption of heavy metals from contaminated areas.

INTRODUCTION

The zeolites are popular collectible mineral groups and important group of minerals for industrial and other purposes. The zeolites are crystalline alumosilicates and alkaline earth metals with three-dimensional structural grid formed from tetrahedrite AlO_4 and $(SiO_4)_2$.Zeolite NaY type belongs to the group of zeolites with a high content of alumo silicatet oxygen tetrahedron and Synthetic zeolites type NaY, analog of natural zeolite foshazit. The mesh of these zeolites are kuboktaeder are colliding through the hexagonal rings D6R. Educated shafts have dimensions from 0,9 to 1,0 nm,. which provides an opportunity for adsorption a number of molecules. Systems channels are filled with water molecules that combine with each other gaps that intersect the alumo silicatet skeleton of the zeolites. The volume of voids in crystals of some zeolites can reach half of their overall volume. Most volume of voids in the crystal lattice determine molecular - sieve properties of the crystals, which depend not so much on the geometry of the channels and the chemical makeup of the crystals, but primarily on the nature and amount of cations that compensate the negative charge of alumo silicatet skeleton. [1,2].

EXPERIMENTAL PART

Adsorption with water vapor depending on the pressure is executed thermostat. Applied is a static pravimetric method. Results are presented in Table 1, 2, 3. Certain areas are specificnite haircut and are 43, 78, 19 m^2/kg 10^3 to 70,37 m^2/kf 10^3 determination. For the specific surface is used the following equation:

$$S = a_m . A_m . 6.023 . 10^3 \, [\, m^2 / kg . 10^3]$$

Tab. 1. Adsorption with water vapor depending on the pressure NaY zeolite + lactic acid – 0,2 mol dm^{-3}, reaction time 2 h at room temperature

P KPa	P/a	am mol/kg	S m^2/kg.10^3
0,1370	0,0314		
0,2999	0,0579	9,7368	70,3769
0,5218	0,0923		

Tab. 2. NaY zeolite previously extracted lactic acid (0,2 $mol.dm^{-3}$) and then with HCl (0,1 $mol.dm^{-3}$), reaction time 2 h, room temperature

P KPa	**P/a**	**a_m mol/kg**	**S $m^2/kg.10^3$**
0,1370 0,2999 0,5218	1,0036 0,0775 0,1192	7,0175	50,7196

Tab. 3. NaY Zeolite + citric acid (0,2 $mol.dm^{-3}$) during 2 h at room temperature reaction

P KPa	**P/a**	**a_m mol/kg**	**S $m^2/kg.10^3$**
0,1370 0,2999 0,5218	0,0314 0,0851 0,1400	6,0576	43,7819

CONCLUSION

The most important use of zeolite Y is as a cracking catalyst. It is used in acidic form in petroleum refinery catalytic cracking units to increase the yeld of gasoline and diesel fuel from crude oil feedstock by cracking heavy paraffins into gasoline gra.de napthas. Zeolite Y has superseded zeolite X in this use because it is both more active and more stable at high temperatures due to the higher Si/Al ratio. It is also used in the hydrocracking units as a platinum/palladium support to increase aromatic content ofreformulated refinery products. [3,4,5]

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CURRENTLY USED PESTICIDES IN SOIL: THEIR FATE AND RISKS FROM THE PERSPECTIVE OF THE TOTAL CONCENTRATION BASED AND THE BIOAVAILABILITY APPROACH

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KEYWORDS
Currently used pesticides, CUPs, bioavailability, bioaccessibility, XAD, silicon rubber, Empore disk

ABSTRACT

Pesticides used in agriculture represent one of the largest inputs of chemicals to soil. Currently used pesticides (CUPs) are a group of chemicals with various physico-chemical and environmental properties. Their input has reached 2×106 tons/year and is expected to even increase. Nowadays, risk assessment associated with the presence of a chemical in soil is based on the total concentration although evidence has been collected that total soil concentration does not properly reflects the environmental risks as it does not allow the factor of bioavailability/bioaccessibility to be considered.

Fig. 1. Pre-cleaned Empore disk (1/4)

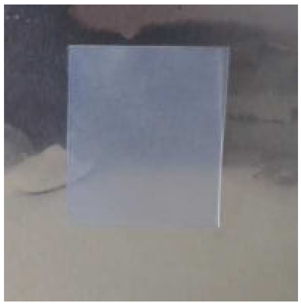

Fig. 2. Pre-cleaned silicon rubber

Fig. 3. Experimental setup with XAD

In this study, the total concentrations of pesticides in soil with their bioaccessible concentrations assessed by three non-exhaustive extraction techniques using sorbents (namely Empore disk (Fig. 1), silicon rubber (Fig. 2) and XAD (Fig. 3)) operating under infinite sink conditions were provided. After the optimization of the extraction time and sorbent amount, soils either with natural occurring residues or spiked to desired concentrations were exposed to the above mentioned sorbents and data on the total amounts and bioaccessible fractions compared over a range of pesticides (including non-polar, polar and ionizable currently used pesticides) and soils with varying physico-chemical properties.

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BROWNFIELDS IN THE PROCESS OF ENVIRONMENTAL ASSESSMENT

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KEYWORDS
Brownfield, Environmental Impact Assessment, Banská Bystrica

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ABSTRACT

Brownfield (contamined site) is in terms of Geological Act defined as pollution caused by human activity, which constitutes a serious risk to human health or the rock environment, groundwater and soil, with the exception of environmental damage. It represents a wide range of areas contaminated by industrial, military, mining, transport and farming, but also to inappropriate waste management. Systematic identification of contaminated sites in Slovakia was solved in 2006-2008 as a project of geological task. The aim of this paper is to focus on assessing the cumulative effects of various negative environmental impacts of contaminated sites in the country based on the Act 314/2014 Coll on the Environmental Impact Assessment and of the assessment activities (Annex 11 of the Act), which may be in terms of the time flow „ex post“, it means in earlier activities carried out, or „a priori“, it means assessment of future (planned) activities. Assessment of the environmental risk of contaminated sites is done on the example of one district Banská Bystrica, in an ArcMap 10 software, where the databases of selected components of the environment were created. Summing up all the points for each brownfield site we got resulting score which was compared with the results obtained by geological survey of SAŽP (geological characteristics of brownfields). From these source data we created final assessment tables and maps outputs.

INTRODUCTION

Slovak Republic regarding the global trend of advanced countries recognizes the principle of sustainable development that integrates the environment into every sphere of social life. Among the important priorities of government activities in the environment include the elimination of environmental burdens which cause increasing contamination of soil, surface, groundwater, air pollution and negatively affect the quality and comfort of life in their neighborhood.

Based on preliminary studies and estimates, there are about 30,000 potential pollution sources. Systematic inventory of environmental burdens (EZ), implemented the project called "Systematic Identification of Contaminated Sites in SR" in 2006-2008 and "Regional assessment studies of environmental impacts on the environment for the selected (region)" in 2008-2010.It was found that 1845 site poses a significant risk to human health and the environment. In particular, the industrial sites, where there was a long hidden and uncontrolled release of hazardous substances in the environment; high-capacity farms; railway yards; uncontrolled landfills of hazardous waste; unsecured warehouses pesticides; fuel and other hazardous substances; pollution caused by the armed forces; extraction of minerals and other activities during which an uncontrolled handled with hazardous substances. These substances persist in the environment, pollute its individual components and negatively affect the health of the population in their neighborhood. They are "time bombs" in the environment, which must be removed or defused.

Current legislation in the field of environmental protection covers all the basic components of the environment and also covers the prevention of pollution and affecting of these components.

This work tries to involve Environmental Impact Assessment as an effective tool to deal with environmental problems. EZ characteristic according to the methodology of Slovak Environment Agency (SEA) were supplemented with the environmental characteristics of the components of the environment - water, soil, landscape, climate, population. Using methodology of scoring, we have identified environmental burdens, which in terms of environmental impacts have the highest impact to the environment.

MATERIAL AND METHODS

EIA as a tool for environmental impact assessment of contaminated sites

Environmental assessment as required legislative tool provides comprehensive environmental, technical evaluation of the impact of buildings, facilities and other activities on the environment. The role of the EIA is according [4]Methodology, Scoping and Guidelines (1981) creating the outline how to get the base of information during the evaluation and application of different methods that ensure a certain approach, gathering, analyzing and interpreting information to the objective pursued. This is a whole range of partial tasks such as:

a) the selection of impacts to be evaluated,
b) prediction of impacts potential without determining their size,
c) an assessment of impacts in terms of their relative importance (weights),
d) comparison and sorting of variants regarding their effect on environment,
e) layout and presentation of impacts of matched variants.

Impact Assessment ([5]Říha, 1995) may be in terms of the timeflow ex post, eg. at first realized activities (environmental burdens), or a priori, which means the assessment of future (planned) activities (remediation or reclamation of environmental burdens).

According to [6]NEPA (1978), the EIA report essentially consists of four parts:

- Analysis,
- characteristics of the factors and components of the current state of the environment,
- a description of the proposed activities,
- impact assessment of projects on the environment (includes a list of all of the environmental impact assessment and their scope, significance both individually and collectively in combination).

The process of EIA use a variety of methods from various disciplines, as well as special planning and forecasting methods in recent years, in particular are prioritized modeling techniques ([7]Hraško, 1997; [8]Kozová et al., 1996).
Tocreate the matrix of vulnerability of environmental factors, it is necessary to define their sensitivity range. For that purpose we used [9]Roberts (1991), a five-level scale.

Tab. 1. Sensitivity range evaluation of environmental factors

Point evaluation	**Verbal rating**	**Description of the impact extent**
5	Critically vulnerable	Realization of the activity causes the loss of environmental parameters with no possibility of relocation, rehabilitation, or restoring. Loss is permanent and irreversible. This category includes parameters such as the critically endangered species, deficient non-renewable resources, unique historical and archaeological sites.
4	Very vulnerable	External pressures caused severe, long-lasting damage and possible loss of environmental parameters. Relocation, renovation or restoration will be very difficult, expensive and will require more than 10 years. This category includes parameters such rare species deficient renewable or difficult the reach to these resources. Actions causing economic problems of the majority of citizens.
3	Middle vulnerable	External pressure causes destruction or disturbance of environmental parameters. Removal or restoration is possible, although will be difficult and expensive and can lastup to 10 years. This category includes environmental parameters as protected species, collapsing or deficient resources and major changes in transport infrastructure.
2	Less vulnerable	External pressure causes less damage and temporary disruption of environmental parameters. Recovering or restoring are possible using natural or artificial tools, and will require less than four years.
1	Not vulnerable	External pressure causes a temporary disruption of environmental parameters. These parameters are the most tolerable to human activities. Recovery is spontaneous and quick, restoring or relocation easy, using conventional tools.

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In the matrix of vulnerability factors of the environment is for each environmental factors as signed level of vulnerability, depending on the intendedactivity or process caused by assessed activity. According Hraško (1997) synthesis of the ecological carrying capacity can be obtained, for example using cartographic method of overlaying vulnerability maps of individual components of the environment or directly entering data into the map. Another approach provides computer processing information (eg. Using Geographic Information Systems - GIS). Its purpose is to detect places in the affected area with a high degree of vulnerability. They are also the place with the most likely transmission changes between the aquatic environment.

Tab. 2. Environmental characteristics identified for the EIA evaluation of environmental burdens

1. The geological environment and relief	A) Geology
	B) Geomorphology
2. Climatic characteristics	A) Climatic characteristic of districts in the relation to EZ
3. Soil	A) Relation of the EZ to soil, soil types
	B) Relation of the EZ to soil B1) Quality parameters B2) Inactivation of pollutants
	C) Soil contamination
	D) Cadmium contamination
	E) Heavy metals contamination
	F) Sulphur contamination
	G) Environmental riskscaused by abiotic components
4. Landscape - structure, stability, protected areas	A) The relative expression of ecological stability by elements of the current landscape structure
	B) Relation of EZ to protected areas
	C) Land cover
	D) Ecological quality of the spatial structure of the country
	E) The ecological significance of the area
	F) Relation of EZ to suitability of dumping
	G) Human, natural-anthropogenic and natural stressors to natural environment
	H) Suitability of the current land use
	I) The ratio of high environmental quality space per capitain the natural-residential sub-region
	J) The ecologicalquality of the natural-residential sub-regionalstructuresbyuse
	K) Relation of EZ to environment quality
	L) The share of high environmental qualityspaceper capitain the EU
5. Population and its activities	
5.1. Health, well-being and quality of life	A) Load districts stressors
6. Water management	A1) Threat of ground water pollutants
	A2) Groundwater pollution-pollution level with Cd
	B) Relation of EZ to water sources protection

RESULTS

When creating environmental documentation in a report on evaluation - assessment of the state of the environment - need to deal with the requirements of the vulnerability and the ecological carrying capacity of the affected area. We have chosen the following procedure. For each componentor environmental factors (described in Table 2), have its own map (a basis for the development have been drawn from the Landscape Atlas of the Slovak Republic, these rvernipi.sazp.sk) in ArcMap10 which relates the elements of the environment to environmental load characteristics. At present in the information system there is registered about 171 assessed activities. Example of the result is shown in figure one and two.

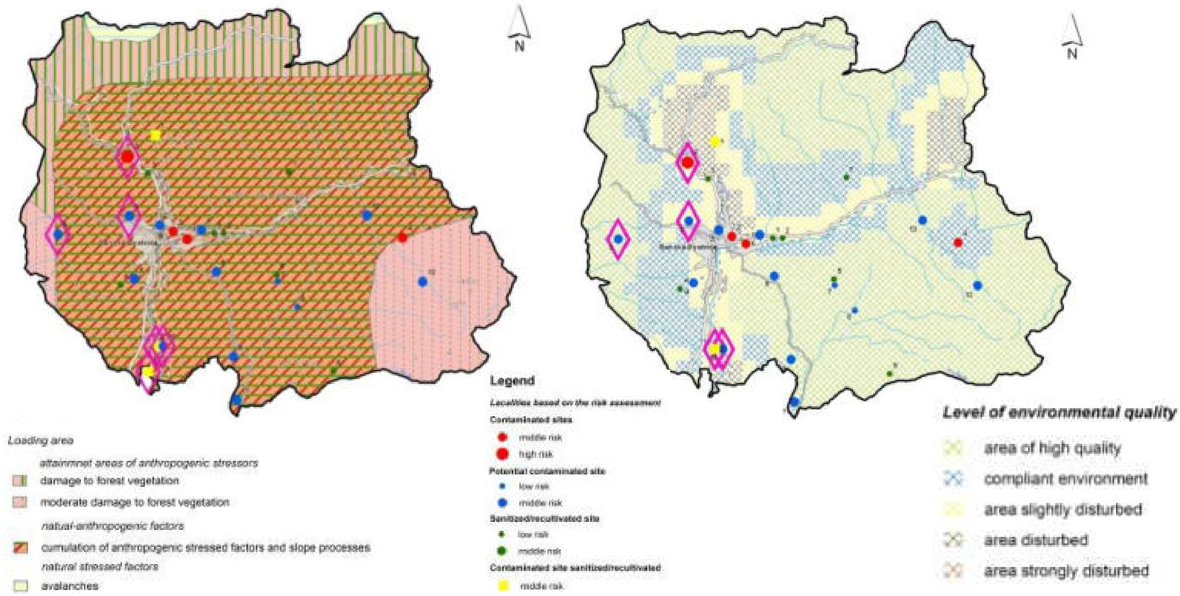

Fig. 1. Load of the impact of human, natural and anthropogenic and natural stressors
Fig. 2. The quality of the environment in relation to the environmental burden

The layer of contaminated sites covered by a layer with the layer loading the impact of human, natural and anthropogenic and natural stress factors defined the characteristics of the various environmental burdens in the district. This relationship was expressed by the score of the two categories of load that overlap with a layer of environmental burdens: accumulation of anthropogenic stress factors and slope processes, which has been allocated -5 and slight damage to forest vegetation assigned the value -3. The layer of contaminated sites covered by a layer with the layer quality of the environment, this characteristic was defined for individual environmental burdens in the district. This relationship was expressed by the score of -4 for the deteriorated environment, -3 for moderately deteriorated environment, -1 for satisfactory environment, 0 for high-quality environment.Interval values achieved for each contaminated site relating to soil in the district of Banská Bystrica is in the range from -14 to -26 points. . The interval of values obtained for contaminated sites related to the water in the region Banská Bystrica is in the range of -2 to -10 points. In summary EZ assessed in relation to the land in the district of Banská Bystrica, the range of points ranging from -47 to -29. The evaluation summary EZ in the EIA process (Annex 11 of the Act 314/2014 Coll on the Environmental Impact Assessment and of the assessment activities), the range of points for potential contaminated sites is -78 (Sásová) to -53 (Ponická cave), for the contaminated sites - 80 (Uľankaarea) to -62 (Ľubietova-Podlipa) and the sanitized/ recultivated localities from -89 (Petrol station Partizánskaroad) to -54 (Ponies - landfills). The results achieved during the environmental risk assessment of contaminated sites were different results, which were detected within solving geological task of Slovak agency of environment. Sites that showed no significant risk levelwithin the geological characteristics, at the inclusion of environmental characteristics have changed for sites that should be priority solved regarding the environment. Including environmental characteristics in terms of dealing with environmental problems should be a crucial process in the identification of related risk in the country. As it is apparent from the principles and priorities of the State Environmental Policy in which we are committed to tackling this issue in accordance with sustainable development. The characterization of the state of pollution in the environment in relation to the environmental load process is extremely difficult and nouniversal valid methodology is available to be able to objectively consider the cumulative efficacy of various negative impacts (environmental, not only geological) and therefore supporting documents became Act 314/2014 Coll on the Environmental Impact Assessment and of the assessment activities, Annex 11, Part B and C. This study also highlights other legislation that affects contaminated sites solutions in order to achieve an Integrated Prevention and Pollution Control Act no. 39/2013, which emphasizes the prevention of pollution, to reduce emissions to air, water and soil, to minimize waste generation and recovery and disposal of waste in order to achieve a high overall level of environmental protection.

CONCLUSION

The aim of this paper was to focus in solving the cumulative effects of various negative environmental aspects of contaminated sites in Banská Bystrica district based on Act 314/2014 Coll on the Environmental Impact Assessment and of the assessment activities (Annex 11), which may be in terms of the flow of time ex post, eg. with more of the activities performed, or a priori, that is assessment of future (planned) activities. The main goal was achieved through sub-objectives: Environmental analysis of selected components of the environment and the assessment of the environmental characteristics of selected environmental indicators, evaluation of environmental load in relation to soil, to water, to land, to the population and its activities.

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RESILIENCE AS A PHENOMENON IN WATER MANAGEMENT OF POST-MINING LANDSCAPE IN HORNÁ NITRA

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KEYWORDS
water resilience, post-mining landscape, water pollution, Horná Nitra region

ABSTRACT

The research is performed on the post-lignite mining landscape in Horná Nitra region (central Slovakia), where the traditional rural landscape was significantly changed by mining activities. Used method of underground mining has activated surface deformations in researched area of the village Koš. Therefore the studied territory is characterized by artificial terrain depressions that have been gradually filled by precipitation and ground water. Over timesuchcreated wetlands have represented highly valuable biodiversity centers that are declared asregional biocentres and have ambition to be included among Ramsars sites. However, thesewetlands have tonowadays fight against challenges as water pollution caused by illegal waste landfills or desiccation caused by inappropriate land management. The purpose of the research is to increase the adaptive capacity of post-lignite landscape through operating under resilience principles. The research exposes a broad spectrum of investigations that works across spatial planning boundaries and witch actively engage new forms of water management interpretation in post mining landscape.

OBJECTIVES

The research is envisioned as open–endedand brings together two objectives. First, a conceptual framework of water resilience of post-mining landscape is synthetized. Then, the theoretical outcomes are valid in model territory of Horná Nitra region (village Koš).The research is conducted across spatial planning boundaries and its scientific goal is to combine technical, spatial and environmental analyses in a GIS- based outcome, which is transferable to other regions.

BACKROUND THEORY

The research analyses whether the theory of socio ecological resilience might be a valuable approach for water management in post mining landscape. Despite the recent hype in the literature around resilience theory, agreement on key aspects of the concept of water resilience is still missing. Water resilience in general has been variously defined and its conceptualization in recent years has been called “fuzzy and contested”. The water resilience concept utilized in this research draws upon the traditional knowledge, stewardship, time-tested and adaptive management solutions, which can help to meet the complex needs of a changing environment. Simply put, for the water sector, the idea of resilience imply moving beyond the traditional “predict-the-acts” approaches towards much more dynamic and flexible concept.

Following notions should be used to identify system properties that are important for addressing the socio-ecological resilience (Bieling, 2011):

1.Thresholds and regime shifts: at the heart of theory of socio-ecological resilience is the analysis of a system’s variables, and special concern is given to the spatial and temporal scales at which these variables act. Some variables are characterized as slow-moving, for example climate change, water consumption or human values, but on the other hand there are also fast-moving variables as floods, water pollution, or social revolutions. When a system crosses certain thresholds that are specific for each variable, it shifts from one state to another. This process is called regime shift (Bieling et al. 2011; Kinzig et al. 2006; Walker et al. 2006). To avoid water-related regime shifts, it is not enough to manage water by itself. On thecontrary, water management need to manage water in socio-ecological system´s perspective.

For instance, a lake may be able to cope with pollution up to a certain point. Passing this threshold, it can suddenly jump into a state where most of the benefits thus far provided – ranging from drinking water supply, over a habitat function for a variety of species, to recreational uses – drop out. Typically, it is very difficult or even impossible to reverse such regime shift (Scheffer et al. 2001).

2.Adaptive cycles and panarchy. The adaptive cycle (Holling 1973) represents four commonly and subsequently occurring stages of change. The usually slow fore loop is characterized by growth and accumulation. In contrast, the back loop is typical rapid process marked by uncertainty, novelty and experimentation, leading to either destructive or creative change in the system (Rockström, Falkenmark, Folke, et al. 2014). Adaptive cycles include the answer to the question of how to deal with breakdown and renewal.

So far, the research describes the lake ecosystem case mainly from theecological point of view. However, also in this case, the lake is part of thesocio-ecological system, and therefore, it is important to demonstrate theinteraction between societal development and ecosystem changes. The firstexample could be seen in period when water quantity and quality was affected by intensification of agriculture. In the upcoming decades, variousmeasures were taken to improve this water crisis. As a result water managersand other groups had to adapt their methods, and try new approaches(Scheffer, 2001; Carpenter, 1999) that where capable of facilitatingappropriate action. In water management practice, adaptive cycles and therole of adaptability could be clearly seen as crucial step to management ofcrisis.

3. Adaptive co-management and adaptive governance. As core tools in building resilience of socio-ecological systems are seen adaptive management and adaptive governance that are closely aligned but do not means the same thing. To understand the difference between adaptive management and adaptive governance, it is useful to illustrate the gaps. On the one hand, adaptive management see each management step as an opportunity for further adaptive learning, thereby includes uncertainties, i.e. „learning to manage by managing to learn“ (PahlWostl et al. 2007). Adaptive management therefore focuses on methods suchas learning by doing, scenario planning and social learning, with the aim to improve flexibility and to readdress management approaches that might be considered as inappropriate (Pahl-Wostl et al. 2007). The literature on adaptive management (Gunderson 2001; Bieling et al. 2011) is currently seen as converging into a literature on adaptive co-management (Olsson et al. 2004). Adaptive co-management has in turn emerged from adaptive management itself, by combining its iterative learning dimension with collaborative management approaches as emphasized in integrated water management, where rights, responsibilities and obligations are jointly shared. On the other hand, adaptive governance is one aspect of the theoretical movement calling for water management solutions to be socially accepted. Adaptive governance has many different interpretations, but generally refers to the need to move from the conventional view of institutions as static, rule-based, formal and fixed organizations with clear boundaries to one that is more dynamic, adaptive and flexible for coping in disturbances (Pahl-Wostl et al. 2007).

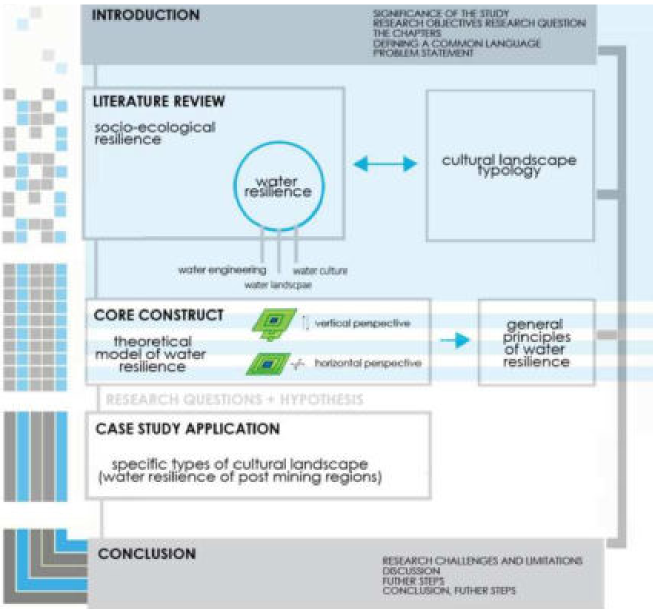
STUDY AREA

Undersurface mining for brown coal and lignite has dramatically altered millions of hectares throughout the Horná Nitra region of central Slovakia. The method of mining used in the region has changed surface landforms in cadastral area between Prievidza and Nováky city, in the researched territory of the village Koš. The studied area is characterized by artificial terrain depressions that have been gradually filled by precipitation and ground water, all as a consequence of underground mining since 1985. The relatively dense system of wetlands has been developed ‘accidentally’ on abandoned landscape between 1975 -1976 and is located in total area of 40 ha. Paradoxically, this is an example how mining industry can also positively impact the biodiversity in environmentally affected landscape. The wetlands represent important regionalbiocentres and have ambition to be declared as Ramsar sites and protected bird´s area. They are especially important for birds, providing vital nesting and migratory areas. However, despite their importance, studies wetlands have to face many challenges. They are polluted at high rate as a consequence of illegal waste landfills, drained because of inappropriate land management or converted to farmlands. Mining activities in the region are continuing, but recultivation process of affected landscape has already started. According to mining law, the territory should be recultivated to its original landform that would mean transformation to agricultural land. Therefore the wetlands call for stronger protection. Inadequate awareness among concerned stakeholders and weak law protection are being accelerated loss of wetland´s resilience. In other words their adaptive capacity is low and could be insufficient when the impacts of climate change or other shocksbecome more and more apparent.

EXPECTED RESULTS

The research aims to produce the following outcomes:

- Develop conceptual framework of water resilience of post-mining landscape
- Develop scenarios of possible future land uses
- Restore the water balance of the studied region
- Protect and spread the original vegetation with mosaic structures (planting hedges and windbreaks)
- Implement system of water retention, filtration and self-purification
- Prevent creation of illegal waste landfills
- Revive natural water cycles in the territory



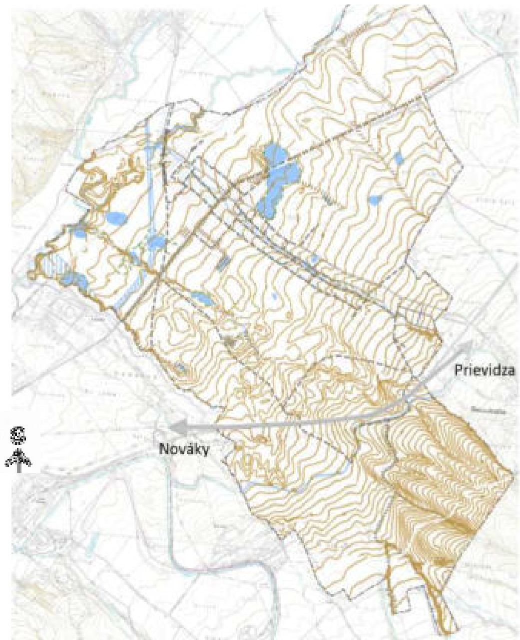


Fig. 1. Research structure (Source: author)

Fig. 2. Location of village Kos and current state of research wetlands that have been changing their shapes and locations depending on mining extraction, ground water table and weather conditions (Source: author)

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EFFICIENCY OF DIFFERENTLY MODIFIED ZERO-VALENT IRON NANOPARTICLES AND THEIR UTILIZATION DURING REMEDIATION OF GROUNDWATER CONTAMINATED BY CHLORINATED HYDROCARBONS

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KEYWORDS
Nano Zero-Valent Iron, Reduction, Biosurfactant, Remediation, Groundwater

ABSTRACT

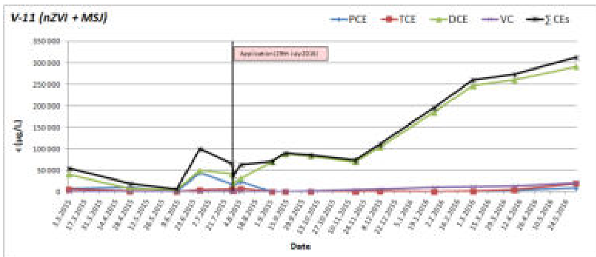
In recent years, nanoparticles of zero-valent iron (nZVI ~ Fe^0) have become a significant remediation material which is increasingly used for the elimination of large amounts of contaminants in a variety of environmental components particularly soil and groundwater environments. Due to the fact that nZVI is "pure" iron (only in zero-valent state) it can be considered as an “environmentally friendly” remediation material. NZVI is characterized notably by ability to induce strong reducing conditions in saturated zone of the soil environment. In water, this material is reactive and acts as an excellent electron donor which makes it a universal remediation material for reductive degradation of many organic contaminants. Among the wide range of substances, which are well degradable by reduction mechanisms, belongs notably group of halogenated aliphatic hydrocarbons. These substances are degraded successfully by mechanism of reductive dehalogenation. Moreover, nanoparticles of ZVI have high migration ability in the soil environment and they can thus treat larger area of contaminated locality. Other advantage of this material is his relatively long-term and progressive reactivity without necessity of further interventions or additions of other reagents. In recent time, there is an effort to focus on modification of nZVI or its combination with other materials (surfactants, biological substrates, carbon etc). These modifications can improve some properties of nZVI (stability, migration in the soil environment, sorption, reactivity etc.). In case of biosurfactants and other biomaterials, these can be additionally utilized by microorganisms as a substrate and start out subsequent biological degradation of residual contamination. This combination seems to be very promising because it can increase efficiency of entire remediation process and simultaneously induces the conditions for subsequent natural attenuation.
Presented study is focused on practical applications of differently modified nZVI during remediation process in area of industrial factory in the Czech Republic. During the in-situ applications, three types of differently modified nZVI (with biosurfactants and in combination with nanocarbon) were used for elimination of chlorinated ethenes in saturated zone of the soil environment on this locality. Not only progress of reduction processes, but also progress of biological activity as a result of present biosurfactants was observed. In order to find out the biological activity in particular boreholes and its affecting by applied materials, a quantitative PCR (qPCR) analysis was used. The analysis was carried out 6 month after application and it was focused on detection of genes encoding enzymes vinychlorid reductase bvcA and vcrA which are capable to degrade chlorinated hydrocarbons. Moreover, identification and relative quantification of the most frequent species of microorganisms (*Dehalococcoides* (DHC-RT), *Dehalobacter* (Dre) a *Desulfitobacterium* (Dsb) capable to degrade chlorinated ethenes were also carried out by the qPCR method. Substantial results relating to remediation effectiveness of particular combinations with subsequent biological activity are compared and presented.
Strongly contaminated area was localized in the locality of former warehouse of chemicals of approx. area about 450 m^2. For this reason, 7 boreholes were drilled into saturated zone of the contaminated area. 6 boreholes (V11 – V16) were used for application of modified nZVI; borehole V10 was chosen as blank borehole. Depth of boreholes was approx. 10-20 m under the surface and the distance between neighboring boreholes was approx. 5 m. Bedrock of the area is formed by low permeable clays and from previous monitoring was found out, that there is not influence between boreholes.
Into each of application boreholes, 5 kg of modified nZVI were applied. For the application, nZVI type NANOFER STAR from LAC, ltd. (Czech Republic) was used. This amount was delivered in barrels as 25 kg of concentrated water suspension. Before the application, the water suspension was diluted by tap water on approx.

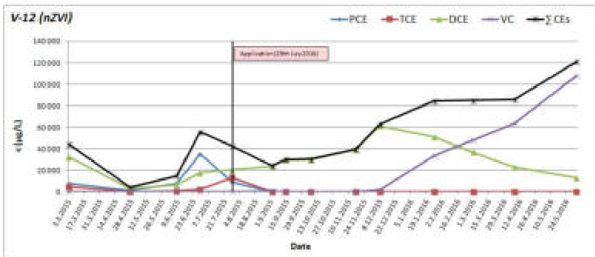
concentration of about 10 g/L and then injected directly into borehole. More detailed information is listed in Tab. 1.

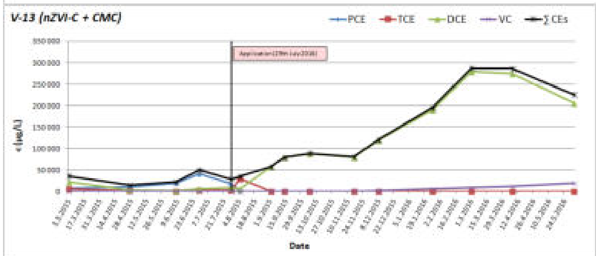
Graphs below (V10 – V11) show substantial results of CEs contamination development before and after the application. Qualitative results from qPCR method and approximate degree of representation of each monitored species in the boreholes are shown in last Tab 2.

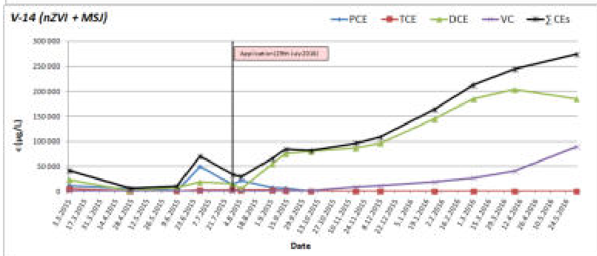
Tab. 1. Detailed information about applied materials

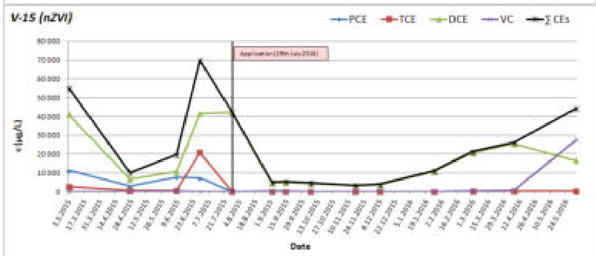
Borehole	Used materials	Adjuvants	Designation	Notes
V-11	nZVI (5 kg) 1)	MSJ (250 g) 3)	nZVI+MSJ	1) nano zero-valent iron (NANOFER STAR, LAC Ltd, CZ) 2) Nanocomposite of nZVI (NANOFER STAR, LAC Ltd, CZ) with carbon nanotubes (RCPTM Olomouc, CZ) 3) biosurfactant on basis of salts of higher fatty acids 4) carboxymethylcellulose 5) served for comparison
V-12	nZVI (5 kg) 1)	-	nZVI	
V-13	nanokompozit nZVI-C (5 kg) 2)	CMC (2,5 kg) 4)	nZVI-C+CMC	
V-14	nZVI (5 kg) 1)	MSJ (250 g) 3)	nZVI+MSJ	
V-15	nZVI (5 kg) 1)	-	nZVI	
V-16	nZVI (5 kg) 1)	-	nZVI	
V-10	*Blank borehole (no application)* 5)			

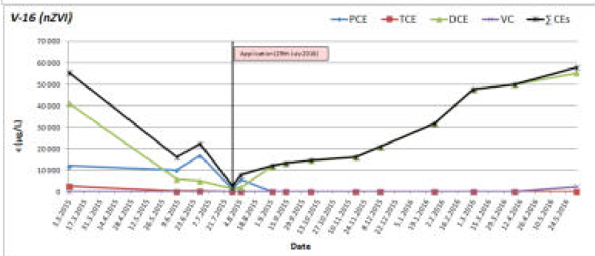


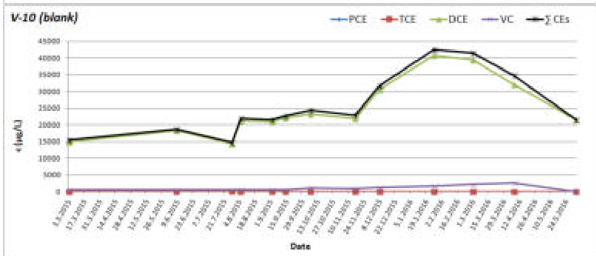












Tab. 2. Results from qPCR method

Borehole	Organohalide respiring bacetria				
	vinylchlorid reductase (bvcA)	vinylchlorid reductase (vcrA)	*Dehalobacter sp.* (Dre)	*Dehalococcoides sp.* (DHC-RT)	*Desulfitobacterium sp.* (Dsb)
V-10	*	**	*	**	**
V-11	***	***	**	***	***
V-12	ND	ND	ND	ND	ND
V-13	***	****	**	***	**
V-14	***	***	**	***	**
V-15	*	*	*	**	*
V-16	*	*	**	*	**

Ed.: Number of asterisks means tentative quantification of detected parameters; ND – not detected

In the all monitored boreholes (except for blank borehole V-10), a significant decrease in oxidation-reduction potential during the first week after application was observed. These changes were observed even 11 months after application. Simultaneously, highly-chlorinated ethenes (PCE and TCE) were completely eliminated during the first week after application. The increase in concentration of DCE (cis-1,2-dichloroethene) has been observed in all boreholes but more significant is this trend in boreholes, where the nZVI was applied with some type of biosurfactant (V-11, V-13 and V-14). The increase in DCE concentration during reductive reactions is natural effect, because highly-chlorinated ethenes (PCE and TCE) are gradually degraded on more stable DCE. Very

significant increase in DCE concentration in case of use of nZVI in combination with biosurfactant is caused by desorption effects of the individual surfactants. This trend will probably last until all of PCE and TCE will not be completely degraded on DCE. Then the degradation of DCE on VC is supposed, as in case of borehole V-12, V-14 and V-15. If the reductive capacity of the nZVI is sufficient, it can be supposed, that all DCE will be degraded on VC and then even VC degraded up to ethene. However, there will be probably need to support the reduction capacity by other application of nZVI.
The aim of the nZVI modification or its applications in combination with other materials is endeavor to improve and support some of its properties or increase the intensity of remediation in saturated zone of the geological environment. The remediation of saturated zone contaminated by CEs using combination of nZVI with biosurfactants seems to be a very interesting and promising approach. During the application occurs not only the desorption of CEs from the rock environment, which can thus participate in the reductive reaction more easily, but the present biosurfactant may also acts as a substrate for the microorganisms and supports thus subsequent biodegradation in the near area around the application borehole. This study reveals that higher biological activity was indeed observed in boreholes where the nZVI was applied in combination with some type of biosurfactant than in boreholes where the nZVI was applied alone. The presence of carbon nanotubes combined with ZVI predicts the possibility of rapid sorption of contaminants in the first step and their subsequent reduction due to presence of nZVI, however, this assumption has not been confirmed so far.

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AUTOTROPHIC DENITRIFICATION USING *THIOBACILLUS DENITRIFICANS* - COMPARISON OF BATCH REACTOR AND FLOW-THROUGH REACTOR

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KEYWORDS
Batch reactor, denitrification, flow-through reactor, nitrates, nitrites, sulphur, *Thiobacillus denitrificans*, wastewater.

ABSTRACT

Thiobacillus (T.) denitrificans belongs to group of gramnegative (**Fig. 1**), chemolithoautotrophic and facultative anaerobic microorganisms. It is widely distributed microorganism, found in soil and water habitants. In terms of environmental, these organisms are very important - they can be used in processes of alternative methods of removing nitrates from contaminated water. *T. denitrificans* can obtain energy by the oxidation of elemental sulfur and certain other sulfur-containing inorganic compounds while electrons are released. Under anoxic conditions, nitrate and nitrite ions are reduced by these electrons and molecules of gaseous nitrogen are formed. Bacteria *T. denitrificans* was cultivated in liquid S6 medium. Its content is shown in **Tab. 1**.

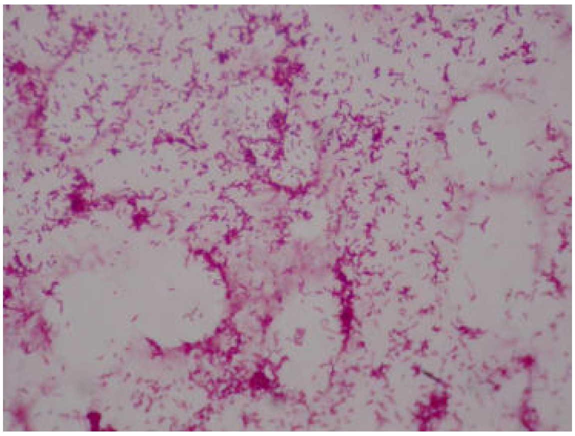

Fig. 1. Gramnegative cells of T. denitrificans, magnified 1000x

In this contribution, we focused on the comparison of denitrification processes in batch reactor and flow-through system and on the comparison of optimum conditions for bacterial cells and denitrification processes. For all experiments, the elemental sulfur was used as electron donor and limestone for pH control. Nitrate and nitrite ions were removed from model sample of contaminated water, which contained nitrates and monosodium phosphate.

Tab. 1. Content of S6 medium for growth of *T. denitrificans*

$Na_2S_2O_3$	10.0 g/L
KH_2PO_4	11.8 g/L
Na_2HPO_4	1.2 g/L
$MgSO_4.7H_2O$	0.1 g/L
$(NH_4)_2SO_4$	0.1 g/L
$CaCl_2$	0.03 g/L
$FeCl_3$	0.02 g/L
$MnSO_4$	0.02g/L

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RESULTS OF THE POPS PESTICIDES POLLUTION IN SLOVAKIA

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KEYWORDS
Pasticides, agrochemical warehaus, risc analysis, POPs

49 environmental burdens coused by the storage and distribution of agrochemicals are registrated in Slovakia Information System of Environmental Burdens (ISEB). 43 of there are registrated in register A (potential environmental burdens), 2 are registrated in register B (environmental burdens) and 6 are registered in register C (remediated and reclaime sites). 23 sites were detailed examined. The gological surveys were conducted within the projects „A Survey of Environmental Burdens In Selected Localities Of The Slovak Republic“ and „Potential environmental burdens – research in selected areas of the Slovak Republic“. 5 sites were indicative examined within project „Management of sites containing POPs mixtures or pesticides in the Slovak Republic“. Location of burdens are presented in Figure 1. The results of the surveys are presented in Table No 1.

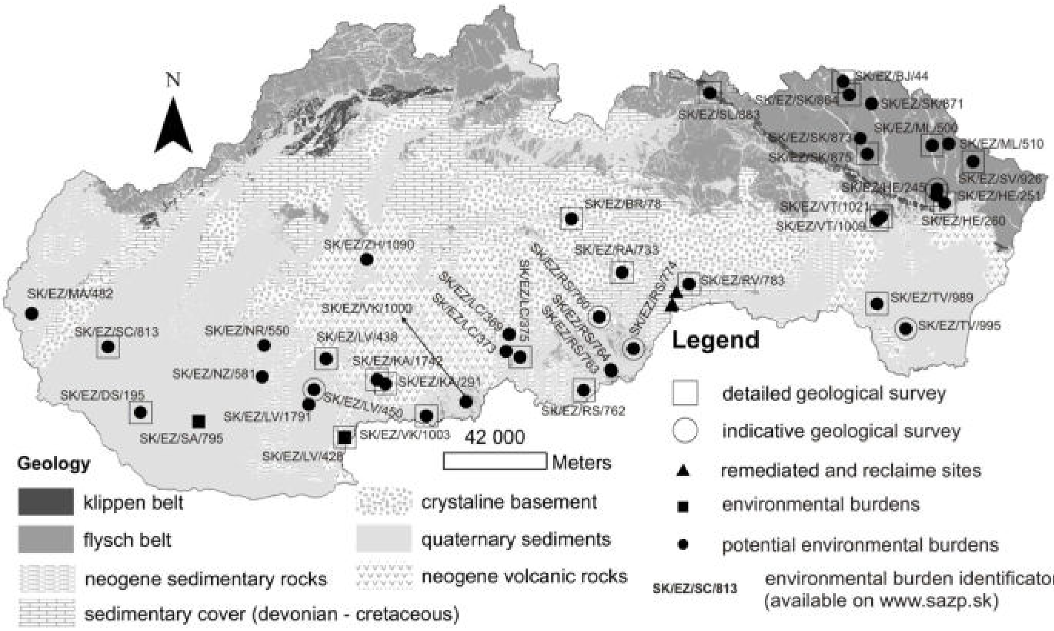

Fig. 1. Location of burdens.

Tab. 1. The results of geological surveys

Contaminated site identificator	Count of pesticide indicators analyzed in GW and S	Detected chemicals over ID	Environmental (ER) and human risc (HR)	Literature	Contaminated site identificator	Count of pesticide indicators analyzed in GW and S	Detected chemicals over ID	Environmental (ER) and human risc (HR)	Literature
SK/EZ/BJ/44	43		no	9	SK/EZ/LC/373	45	lindane (GW)	no	9
SK/EZ/BR/78	44	–	no	10	SK/EZ/RS/762	44	atrazine (GW)	no	17

Contaminated site identificator	Count of pesticide indicators analyzed in GW and S	Detected chemicals over ID	Environmental (ER) and human risc (HR)	Literature	Contaminated site identificator	Count of pesticide indicators analyzed in GW and S	Detected chemicals over ID	Environmental (ER) and human risc (HR)	Literature
SK/EZ/DS/195	44	–	no	11	SK/EZ/VT/1021	45	DDT (GW)	no	24
SK/EZ/HE/245	37	–	–	3	SK/EZ/LV/438	127	lindane, acetochlor, chloridazon-desfenyl, metolachlor (GW)	ER (chloridazon-desfenyl)	27
SK/EZ/HE/251	45	–	no	12					
SK/EZ/HE/260	38	–	no	1					
SK/EZ/KA/291	44	–	no	13	SK/EZ/SC/813	216	p,p,-DDD, lindane (GW, S), o,p,-DDD, p,p-DDE, p,p,-DDT (S) alfa, beta-HCH ,fensone, butylate, benzothiazuron, malaoxon, metolachlor (GW)	ER- no HR: CVRP (DDE) - child, adult CVRP (DDT, DDD) child	28
SK/EZ/LV/428	14	–	no	26					
SK/EZ/LV/450	37	–	–	6					
SK/EZ/ML/500	44	–	no	15					
SK/EZ/RA/733	43	–	no	16					
SK/EZ/RS/760	37	–	–	4					
SK/EZ/RS/774	37	–	–	7	SK/EZ/TV/989	226	methiocarb, atrazine, chlorthal-dimethyl, metolachlor (GW)	no	25
SK/EZ/RV/783	44	–	no	18					
SK/EZ/SK/864	45	–	–	19					
SK/EZ/SK/875	44	–	no	8	SK/EZ/VT/1009	45	atrazine (GW) chlorthal-dimethyl, methiocarb (S)	no	23
SK/EZ/SL/883	44	–	no	20					
SK/EZ/SV/926	45	–	no	21					
SK/EZ/TV/995	37	–	–	5	SK/EZ/KA/1742	13	–	no	2
SK/EZ/VK/1003	45	–	no	22	Legend	(S) - soil, (GW) - groundwater, ID - indicator criterion,			

The table shows that of the 23 sites that were examined at the stage of detailed survey, pesticides occurred in environmental media over ID kriterium (limit prescribed concentration of a pollutant for the soil, rocks and groundwater beyond which can endanger human health and the environment, ie. this calls for monitoring of contaminated sites) in 7 sites. Of these, the one site presents environmental risk (showed risk analysis) from the substance chloridazon-desphenyl and at one location became a health hazard due to DDE, DDT, DDD (showed risk analysis).

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THE IMPACT OF A FLOOD ON THE CONTAMINATION OF THE AGRICULTURAL SOILS – A CASE STUDY OF FLOOD EVENT IN THE CZECH REPUBLIC IN YEAR 2013

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KEYWORDS
fluvisols, contamination, soil, floods, soil bioassays

INTRODUCTION

Alluvial soils (fluvisols) along the rivers usually belong to the most fertile soils used for agricultural purposes. In the Czech Republic, fluvisols cover about 6 % of agricultural land. However, their importance in food production is much higher, because the 75 % of fluvisol areas is the fertile arable land (Skála et al. 2013). Fluvisols are naturally formed by transportationof sediment and its deposition in floodplain areas during flood events. Sediments could delivernot only significant amounts of nutrients (organic matter, phosphorus, nitrogen,divalent cations, etc.) and clay particles, butcould potentially serve as a secondary source of contamination for the fluvisolsand other flooded areas (Schwartz et al. 2006). Contamination of highly fertile fluvisols can markedly limit their agricultural use (Vácha et al. 2013). More frequent occurrence of stronger floods in Europe in recent years increases the need for the assessment of regularly flooded areas in order to understand and predict the possible toxicological and ecotoxicological consequences of such events (Wölz et al. 2008). The present study aimed to define the impact of the flood event in year 2013 on soil characteristics, contamination and ecotoxicity in the agricultural soils in Bohemia regions in the Czech Republic.

MATERIAL AND METHODS

A total number of twenty-three soil samples from agricultural soil located in Bohemia regions (Labe, Berounka and Ohře) in the Czech Republic were collected.Soil sampling was performed before (during years 2011 and 2012) and after flood event in year 2013. Samples were collected from the tilled depth (0–20 cm) with a manually operated stainless-steel spade. Soil samples were characterized for physicochemical parameters (pH, TOC, particle size distribution), concentrations of heavy metals (As, Cd, Cu, Hg, Ni, Pb, Zn), aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), hexachlorocyclohexane (HCH) and dichlordiphenyltrichloroethane (DDT). The ecotoxicity of soil samples was evaluated by *Enchytraeus crypticus* reproduction test (ISO 16387, 2014), *Folsomia candida* reproduction test (ISO 11267, 2014) and *Lactucasativa* root growth test (ISO 11269-1, 2012).

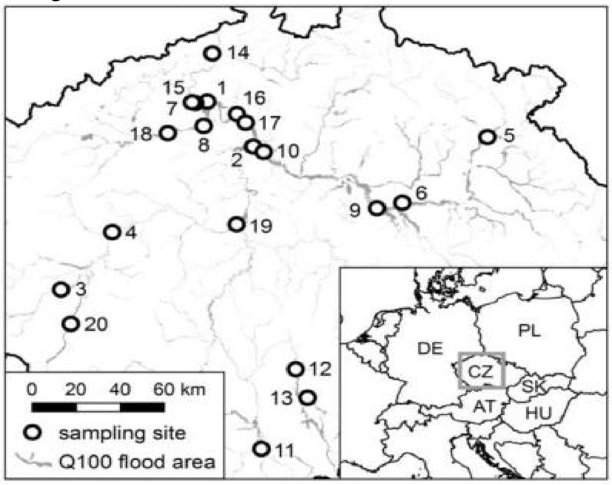

Fig. 1. Distribution of sampling points in Bohemia regionsin the Czech Republic.

RESULTS AND CONCLUSIONS

In general, the flood event did not lead to significant changes insoil characteristics. The impact of flood on soil contamination varied among localities and both decrease and increase of contamination levelswere observed. Preventionlimit values for agricultural soils(Czech Decree no. 153/2016 Coll.)wereexceededat nine localities after flood event in 2013. Increased soil contamination was mostly connected to local sources, i.e. chemical facilities. The highest increase was recorded in case of PAHs and DDT. Moreover, flood had tendency to increase mobility of metals (As, Cu, Ni, Zn). At four localities, flood event decreasedsoil contaminationbelow the prevention limit values (Czech decree 153/2016 Coll.). Very low DDT concentrations (lower than 2 mg/kg) were detected at three localitiesafter the flood. The results of this study show the importance of incorporation the fluvisol contamination in the risk assessment focused on flood effects.
The results of *Folsomia candida* reproduction bioassay and *Lactucasativa*root growth test correlated with metal content (Hg, Ni, Pb, and Zn) in soil samples. *E. crypticus*showed sensitivity to organic pollutants (HCH and PAHs).The results of this study corroborate that performed soil bioassays could be useful to complement the chemical analysis.

ACKNOWLEDGEMENTS

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FROM CONTAMINATED SITE TO ATTRACTIVE RECREATIONAL HEART; QUARRY IN DEVÍNSKA KOBYLA

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KEYWORDS
revitalization, gudrons, recreation, protected nature, learning landscape design, sustainability

This study explores the process of prospective cultivation towards sustainable development of originally contaminated site of old quarry in protected hilly massif Devínska Kobyla belonging to Little Carpathians in Bratislava. The quarry Srdce (Heart) located in direct contact with popular recreational locations was great environmental burden after it was used as a repository for hazardous waste products gudrons exported from the Apollo refinery during its liquidation in the 1960s. After ordering remediation of contaminated site by the Ministry of Environment of the Slovak Republic were gudrons and contaminated soil excavated, completely eliminated and terrain was re-planting in 2014-2015. This research deals with the overall sustainable development of unique surrounding areas by integrating the quarry in recreation network of Devínska Kobyla. Because the site has potential not only to dispose of being the environmental burden, but is poised to become the heart of recreation in the locality where existing recreational infrastructure hardly resist public pressure. The design builds on previous research and landscape-planning project dealing with humanization of Devínska Kobyla developed by author in cooperation with Daphne NGO and it offers the vision how to transform contaminated site to attractive recreational core contributing to sustainability of whole locality.

Fig. 1. The quarry Srdce during remediation of contaminated site, Source: TASR, 5. Feb. 2015
Fig. 2. The quarry Srdce after revitalization - gudrons and contaminated soil were excavated, Source: TASR, 14. Dec. 2015

The quarry „Srdce“ („Heart“), located really in the heart of hilly massif Devínska Kobyla, was only few monhs ago deprived of the great ecological burden – the gudrons. As the site is situated in close proximity to several boroughs of Bratislava, the need for recreation in the locality is great. Even more when the nearby western part of Devínska Kobyla is highly protected, and many forms of active recreation are excluded from there. The aim in this natural environment is then to create a logical transition and to better connect urban and natural recreation landscape.

It is therefore essential to create a structure and hierarchy the Devínska Kobyla natural areas in Bratislava urban fringe, especially highlight the most important, key areas with the biggest potential - as the quarry Srdce. The system should connect main entry points from settlement with few main cores for recreation, where the major interest of urban population focuses. In the quarry, various functions could cumulate – the center for sport and play activities, picnic areas. By using learning landscape design and land-art objects, also the education in nature can be involved to these activities. It will help not only to deepen genius loci of locality and its artificial value, but it will also attract broader spectrum of visitors to this locality; and the quarry Srdce will really overflow with life.
This would help to not only improve the quality of recreation of visitors in nature, but mostly it will improve the regulation and preservation of highly protected nature from unappropriate activities.

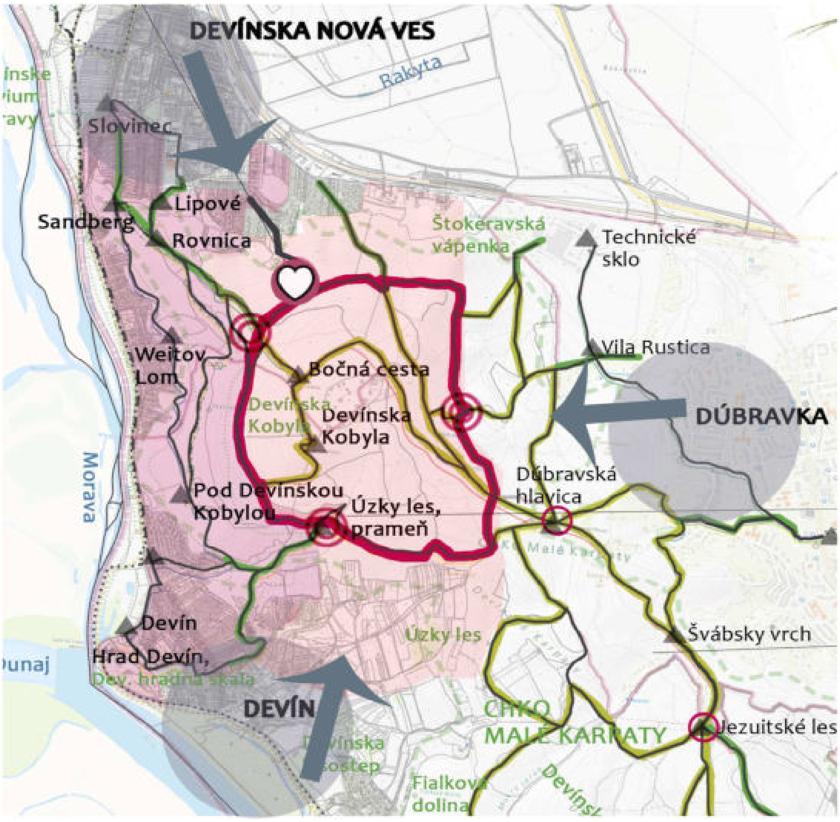

Fig. 3. The connection of trails to systematic infrastructure for recreation; revitalized quarry Srdce as the main buffer zone and center for recreation for residents and visitors from Devínska Nová Ves, Source: author

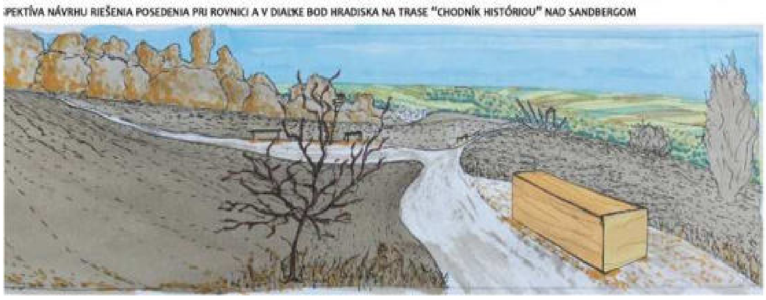

Fig. 4, 5, 6. Learning landscape design-sketches of recreational areas and interactive objects designed for Kobyla by author
Fig. 7. Learning landscape design in Devínska Kobyla, applicated by Daphne NGO

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THE REHABILITATION OF A POLLUTED SITE WITH THE SOIL VAPOR EXTRACTION (SVE) METHOD

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KEYWORDS
Soil vapor extraction treatment, SVE, pollutedsoil, hydrocarbons, kerosene, fuel station, VOC

ABSTRACT

The treatment of polluted soil by vapor extraction has more advantages than the conventional method of soil remediation,e.g. by excavation and treatment of polluted soil in soil decontamination centers. Even if the duration of the treatment of the polluted soilin this caseis superior to the traditional method by excavation, the technical possibilities during the treatment are larger (the construction of a building on the spot is allowed, etc.), the costs are reduced, the risks linked to the deep excavation are reduced to zero, etc. In this article,it will be described the option chosen for the rehabilitation of a fuel-station in Belgium, by taking into account the difficulties to apply the excavation methods and the treatment ex-situof the polluted soil (the pollution detected during studies down to 22 m deep), the type of the pollution (volatile fractions of aromatic oils), the characteristics of the natural soil (permeability), the size of the site and the use of the site after rehabilitation (need to build new halls of storage and maintenance).

INTRODUCTION AND ROLE OF SPAQUE

In 1991, the Walloon Government (Belgium) decided to create a public company in order to solve the landfill's environmental issuesand to manage the brownfields rehabilitation. Since its creation, SPAQuE has managed several hundreds of sites - brownfields, landfills, tyre stockpiles – spread throughout Wallonia. The key strength of SPAQuE is its ability to handle the entire processof site rehabilitation. In 2012 the Walloon Government charged SPAQuE with the rehabilitation of theBierset-Liège Airport site. The rehabilitation of this site was supported also by ERDF founds.

SITE DESCRIPTION AND PREVIOUS WORKS

The site concerned is located within the perimeter of Bierset-Liège Airport (Belgium). This area, called Stapol 4, was used, during the fifties, to receive the installations of the military airfield of Bierset. Many fuel-stations, named Stapol, were built in order to stock in tanks and to distribute the fuel tomilitary planes. The Stapol 4site was composed of five underground tanks and of a small building housing the pump. Each tank had a capacity of 50 m³ and contained kerosene. The pollution identified in the soil under this fuel station consisted ofPetroleum Hydrocarbon and monocyclic aromatic oils (VOCs).
The Stapol 4fuel station has undergone rehabilitation works late 2012, consisting of the removal of fuel tanks and the excavation of the first 3 polluted spots on the first 4 meters deep. These 3 polluted spots were polluted with Mineral Oils, Naphthaleneand Xylenes.
To complement the clean site at lower costs, and to treat the 4^{th} spot polluted with Mineral Oils and Naphthalene, taking into account the fact that the pollution detected during studies went down to 22 m deep, it was establisheda device for vapor extraction and for the treatment of polluted air. The surface of this spot was 550 m^2.
The planned redevelopment project ofthe site consists of the extension of the airport hangar area. This requires to lift up of the sitelevel with 4 m so that to align the level of existing buildings further south. After theseearthworks, the site will be used to build new halls of storage and maintenance; one thereof to be built above the site of the former station. The construction of this hall had to be performed in coordination with the implementation of the pumping well system provided.

WORKS AND EQUIPMENT

The SVE works on site were executedbetween 2013 and 2014 (the duration of work was 5 months), and they consistedof:

- The completion of drilling and equipping of vapor extraction wells;
- The construction and installation of the gas treatment unit.

The treatment consistedof filtration of the extracted soil vapors, in two activated charcoal columns installed in series.

To be efficient, the SVE system needs the following elements:

- Several wells (for extraction, ventilation, observation) connected to a pumping and extractionstation;
- An extraction station and pumping gas flawed. This station comprises an extraction line provided with a condensate separator, a gas turbine and various safety accessories (fast closing valve, anti-flame propagators, etc.), or of measurements (thermometer, manometer, samplings, etc.). This extraction line is connected to the various manifolds from pumping wells. These lines are equipped with control valves, essential for good network management;
- Two mobile activated charcoal filters, each with a capacity of +/- 2 m³ coal, connected to the extraction station through appropriate flexible pipes;
- An exhaust stack gases treated, for returning them in height and prevent them from stagnating near the installation.

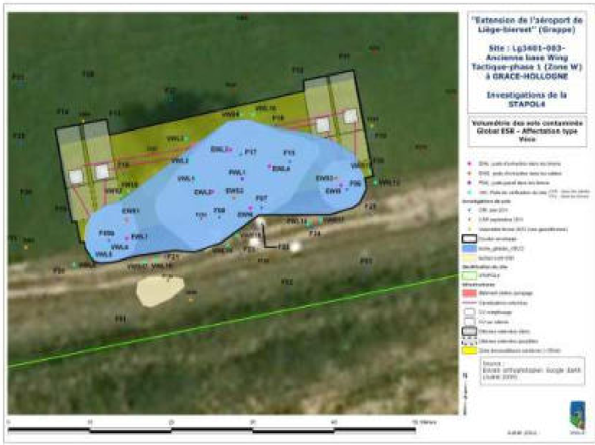

Fig. 1. The location of the pollution and wells on site

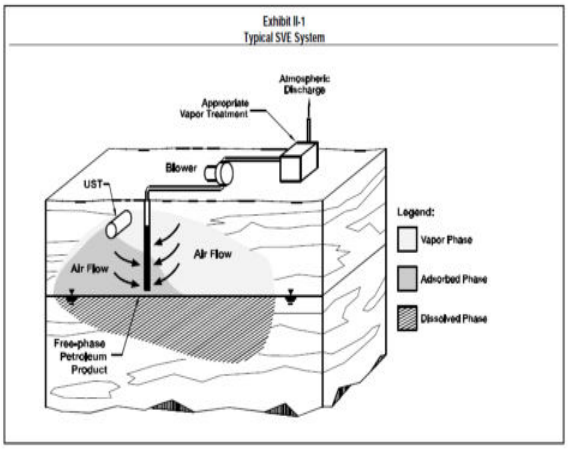

Fig. 2. Typical SVESystem (EPA source-USA)

ADVANTAGES OF SVE AND CONCLUSION

This technology has been proven effective in reducing concentrations of volatile organic compounds (VOCs) and certain semi-volatile organic compounds (SVOCs) found in petroleum products at underground storage tank (UST) sites.

Some advantages of the SVE method are: proven performance, readily available equipment, easy installation, minimal disturbance to site operations, cost competitive, easily combined with other technologies, can be used under buildings and other locations that cannot be excavated. On the other hand, the effectiveness of SVE is less certain when applied to sites with low permeability soil or stratified soils.

The efficiency of SVE treatment is now proved on site, and the costs of this methodare lower thanthose for the excavation of polluted soil, transport to a specific treatment center, and treatmentof the polluted soil. Based on estimations, the SVE treatments have to be done during three years. The initial cost of the installation on site (wells, gas treatment unit, etc.),is around 480.000 € and the cost of the treatment is around 60.000 € per year (including furniture, electricity, active coal, etc.).

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How to evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites – EPA- May 2004

CHEMICAL AND MICROBIOLOGICAL CHARACTERISTICS OF WASTE MATERIAL FROM FISHPONDS IN REPUBLIC OF MACEDONIA

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KEYWORDS
waste material, fishpond, chemical and microbiological characteristics

ABSTRACT

In order to preserve the natural ecological balance of aquatic ecosystems, there is a strong need for prevention of loading the surface and groundwater from contamination by material derived from fishponds. For thispurpose, chemical and microbiological tests of raw and thermally processed waste material were conducted from three fishponds in Republic of Macedonia.

It was found that raw waste material was not contaminated with harmful compounds, heavy metals and pesticides, but contained a lot of microorganisms which makeit unusable.In thermally processed waste material there were hardly any harmful microorganisms and the total number of bacteria was reduced to a minimum. This suggests that thermally processed waste material from fishponds can be used as a supplement to animal food and for other purposes.

EXPERIMENTAL RESULTS

Waste material (sediment) from the basins of three trout ponds in the Republic of Macedonia was collected and chemical and bacteriological analysis were performed. Analyses were performed on samples of raw and thermally treated sediment in the months of June, July and August. Chemical and microbiological analysis were carried out according to the standard methods. Heat treatment of the sediment was conducted at 100^0C for 10 minutes.

Tab. 1. Chemical analysis of raw sediment from three fishponds (A, B, C) (ppm)

Constituents	A			B			C		
	June	July	August	June	July	August	June	July	August
Organic Substances, %	11.30	10.24	10.50	16.22	16.99	17.11	17.04	17.36	18.02
pH	7.40	7.71	7.72	7.61	7.50	7.50	7.33	7.52	7.64
NH_4	0.001	0.004	0.006	0.0007	0.0004	0.0007	0.0004	0.0004	0.0006
H_2S	0.007	0.006	0.008	0.0008	0.0006	0.001	0.001	0.0003	0.0007
Chloride	0.0007	0.0008	0.0008	0.0002	0.0004	0.0002	0.0004	0.0006	0.0007
Nitrites	0.0008	0.0012	0.001	0.0009	0.0008	0.001	0.003	0.003	0.0008
Nitrates	10.0	9.0	6.0	5.1	6.0	5.9	2.8	3.5	5.0
Carbonates	37.0	30.5	30.5	30.0	40.5	37.7	38.0	35.5	30.7
Sulphates	0.0009	0.0007	0.0007	0.0006	0.0009	0.0008	0.002	0.0006	0.0004
Phosphates	0.008	0.008	0.0009	0.0068	0.0054	0.0012	0.0008	0.0005	0.0006

According to chemical analyses raw and thermally treated waste material did not contain harmful compounds, heavy metals and pesticides above the permitted quantities. The presence of lead, zinc, mercury, cadmium, arsenic, chromium and phenols was not determined (Tab. 1 and 2).

Tab. 2. Chemical analysis of thermallytreated sediment from three fishponds (A, B, C) (ppm)

Constituents	A			B			C		
	June	July	August	June	July	August	June	July	August
Organic Substances, %	85.2	85.24	84.06	86.22	86.00	87.14	88.32	87.23	86.75
pH	7.52	7.48	7.46	7.55	7.46	7.47	7.15	7.35	7.42
NH_4	0.0001	0.0001	0.0002	0.0001	0.0002	0.0002	0.0002	0.0001	0.0002
H_2S	0	0	0.0001	0	0	0.0001	0	0.0001	0
Chloride	0	0.0001	0.0001	0	0.0001	0.0002	0	0.0002	0.0001
Nitrites	0.0006	0.0008	0.0008	0.0007	0.0008	0.0007	0.003	0.0006	0.0007
Nitrates	6.0	5.2	4.5	5.0	6.0	5.8	2.8	3.50	5.20
Carbonates	39.0	42.0	35.0	30.0	40.5	37.7	38.0	36.5	37.5
Sulphates	0.0002	0.0004	0.0002	0.0005	0.0007	0.0003	0.001	0.0002	0.0003
Phosphates	0.0003	0.0004	0.0009	0.0060	0.0051	0.0011	0.0007	0.0015	0.0008

Tab. 3. Microbiological analysis of raw sediment from three fishponds (A, B, C)

Microorganisms	A			B			C		
	June	July	August	June	July	August	June	July	August
Salmonella (in 25 g)	0	0	0	0	0	0	0	0	0
Staph.pyogenes (in 0.1g)	0	0	0	0	0	0	0	0	0
Strept.pyogenes (in 0.1g)	6	10	12	0	2	4	4	2	0
Escherichia coli (in 0.01g)	12	10	6	8	7	3	8	5	3
Sulfite-reducing bacteria (in 0.01g)	2	6	5	1	0	3	0	2	1
Coliform bacteria (in 0.01g)	4	3	9	11	7	6	12	9	6
Proteus (in 0.01g)	0	0	0	0	0	0	0	0	0
Pseudomonas aeruginosa (in 0.01g)	0	0	0	0	0	0	0	0	0
Yeasts (in 1 g)	1420	1230	1440	980	810	1210	198	512	340
Molds (in 1 g)	1120	1680	1232	1560	1150	950	480	620	850
Anaerobic bacteria (in 1 g)	0	0	0	0	0	0	0	0	0
Aerobic mesophilic bacteria (in 1 g)	86000	112000	109700	98000	105000	118700	89000	45000	64000
Total bacteria (in 1 g)	100000	132000	107000	159000	122000	134000	121000	98000	102000
Contaminants (in 1 g)	54000	57000	87000	24000	28000	19000	59000	388000	32000

Fresh sediment contained a lot of harmful microorganisms, coliform bacteria and bacteria of the type Escherichia coli, as well as high number of total bacteria, render it unusable. This situation indicates that the waste material, in addition to unused food contained a lot of fish feces (Tab. 3).

In order sediment to be used for feeding the fish and other animals, it is necessary to be recycled through heat treatment. Thermally treated sediment containedafew yeasts (<134/g), aerobic mesophilic bacteria (<3100/g), total number of bacteria (<5520/g) and contaminants (<1120/g). With the heat treatment, despite harmful and other species of microorganismswere eliminated as well. Accordingly, the sediment after heat treatment from chemical and microbiological point of view can be used as a supplement in animal food, especially to complement the protein part of the food.

The bacteriology of pond sediments is largely driven by type of diet added to ponds, ambient temperature and limiting levels of oxygen (Smith, 1998).Disposal of pond sediments to natural systems possess an environmental threat (Funge-Smith and Briggs, 1994;Smith, 1996)and is a waste of valuable nutrients (Lin and Yi, 2003).Lack of scientific documentation on quantitative and qualitative aspects of pond sediment hampers wider adoption and promotion of pond sediment use in agriculture (Gross and Boyd, 1998).

CONCLUSION

Sediment from fishponds after its heat treatment can be freely used as a supplement in animal food and as a fertilizer for various crops.Howeverit is necessary to find practical ways to fulfill and to assess the economic effects of its application.

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ASSESSMENT OF HEAVY METAL CONTAMINATION IN SEDIMENTS FROM THE MAIN RIVERS OF THE MITIDJA PLAIN, ALGERIA

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KEYWORDS
Heavy metals, sediment, quantitative contamination indices, Mitidja plain.

ABSTRACT

The concentrations of heavy metals (Cd, Cr, Cu, Fe, Ni, Pb and Zn) in surface sediment samples collected from the main rivers of the Mitidja Est plain were studied to evaluate their distribution and contamination level. The sediment samples have been subjected to acid digestion using the standard procedure USEPA Method N3050B and concentration of heavy metals were determined by atomic absorption spectrometry. The contamination status by heavy metals in sediment was evaluated based on enrichment factor (EF) and geoaccumulation index(Igeo). In addition, the risks associated with heavy metals accumulation in sediment were assessed using the potential ecological risk factor (E_r^i). The results showed that the mean concentrations of metals in mg kg^{-1} were Cd (3.8), Cr (100.5), Cu (39.6), Fe (44932.4), Ni (51.4), Pb (54.6) and Zn (291.7). The concentrations of the studied metals decreased in the order of Fe >> Zn > Cr > Pb > Ni > Cu> Cd. The results revealed that sediment in this study were very strongly contaminated by Cd, moderately contaminated by Zn and Pb and uncontaminated by Cr, Cu, Fe and Ni. All studied metals showed low potential ecological risk with the exception of Cd. These finding suggested that Cd, Zn and Pb may be attributed to the anthropogenic activities while Cr, Cu, Fe and Ni came mainly from lithogenic sources.The results of this study are importantfor the development of any future management strategies to protect the aquatic environment.

INTRODUCTION

The Mitidja plain has undergone these last three decades urban and industrial growth that could generate increased concentrations of certain pollutants such as heavy metals in the environment. Indeed, Benouar (2002) reported that the main rivers of the plain are often open to waste water that are little or not treated which may weaken the quality of the aquatic environment. Therefore, a good knowledge on heavy metals concentrations in sediments, but also the contribution of both the natural and human activities, is crucialfor the management of the contaminated sites.The geochemical methods through applying quantitative indices such as enrichment factor (EF) and the geoaccumulation index (Igeo) are widely used to search the influence of natural and anthropogenic sources on the degree of sediment contamination by heavy metals.The aim of this study was to assess the contamination status of heavy metals, using the geochemical approach.

MATERIAL AND METHODS

Seventeen sites in the study area were selected for the study of heavy metals concentrations in sediments of the main tributaries of the Mitidja East plain **(Fig. 1)**.The digestion of sediment samples was performed according to the method 3050B recommended by the US Environmental Protection Agency (USEPA, 1996).Several quantitative indices have been proposed in the international literature to assess the level of sediment contamination. These include enrichment factor (EF) and the geoaccumulation index (Igeo). Besides these two indices that allow obtaining information on sediment contamination, ecological potential risk index(ERI) was calculated.

-Assessment according to enrichment factor (EF)

This index is defined as the ratio between the element concentration and the conservative element concentration in the sample and; the element concentration and the conservative element concentration in the reference material.

$$\mathrm{EF} = \frac{(\mathrm{Cn})/(\mathrm{Fe})\ \mathrm{sediment}}{(\mathrm{Cn})/(\mathrm{Fe})\ \mathrm{reference\ material}}$$

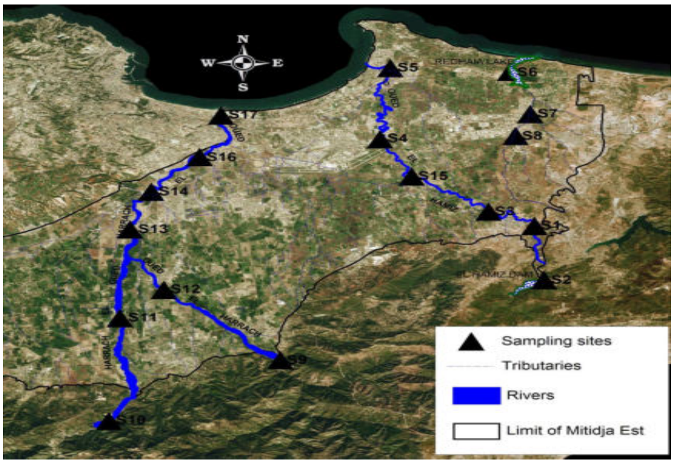

Fig. 1. Localization of sampling sites

-Assessment according to Geoaccumulation index (Igeo)

This empirical index compares a given concentration versus a concentration considered as reference value or geochemical background and can be calculated using the following formula:

$$\text{Geoaccumulation index } (I_{geo}) = \log_2\left[\frac{\mathrm{Csediment}}{1.5\mathrm{B\ reference\ material}}\right]$$

-Assessment according to potential ecological riskcoefficient E_r^i

In addition to compare the measured concentration of the metal in the sediment to the corresponding value in the reference material, the potential ecological risk coefficient takes into consideration the toxicity factor of each metal.

$$E_r^i = T_r^i * \frac{C^i}{C_0^i}$$

RESULTS AND DISCUSSION

The mean concentrations of metals in mg kg^{-1} were Cd (3.8), Cr (100.5), Cu (39.6), Fe (44932.4), Ni (51.4), Pb (54.6) and Zn (291.7). The mean EF valuesindicated that the Cr, Cu and Ni have minor enrichment (EF <2); Pb and Zn have moderate enrichment (2 < EF < 5). The EF results for Cd (20<EF< 40) are the highest among the metals and it has very high enrichment. The meanIgeo results showed that the surface sediments were uncontaminated with respect to Cr (-0.42), Cu (-0.03),Fe (-0.28) and Ni (-0.41). The mean value of the Igeo of Pb (0.82) suggested that the sediments of the study area were uncontaminated to moderately contaminated by this metal, and moderately contaminated with respect of Zn (1.30). In relation to Cd (4.51), the sediments were strongly contaminated by this element. Risk assessment based on the potential ecological risk coefficient showed that all elements have a low ecological risk with the exception of the Cd ($E_r^i > 320$).The concentrations of Cd, Pb and Zn increase as a result of some anthropogenic activities in the study area.

CONCLUSION

The application of enrichment factor as well as the geoaccumulation index revealedthat the concentrations of Cr, Cu and Ni were derived mainly from natural process. Other elements Cd, Pb and Zn in the sediment were primarily from anthropogenic activities. Among all the elements, Cd was the most potential ecological serious risk metal.

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THE POSSIBILITY OF PHYSICAL METHODS APPLICATION FOR ELIMINATION OF PRODUCER MICROORGANISMS IN GROUNDWATER AFFECTED BY SURFACE WATER

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KEYWORDS
Groundwater, Microscopic particulate analysis, *Desmodesmus subspicatus*, FAR emission, UV emission

ABSTRACT

Groundwater influenced by surface water contain various pollutants as different substances and microorganisms. Any water beneath the surface of the ground with:

1. significant occurrence of insects or other micro-organisms, algae or large-diameter pathogens such as Giardia lamblia or
2. significant and relatively rapid shifts in water characteristics such as turbidity, temperature, conductivity, or pH which closely correlate to climatological or surface water conditions (GWI – MPA, 2003).

Microscopic particulate analysis is the method to identify that kind of risk. Ones of the relevant indicators are algae. Producer's organisms are organisms that clearly come from surface water. These organisms do not belong to an extremely risky from the point of human health. However, decomposition of organic matter may become secondary source of risky microorganisms and in the ground water are able to survive for several weeks or months. In this study the attention was paid to selected algae species that were exposed to various types of radiation. Radiation under certain conditions does not necessarily mean inactivation of the autotrophic organisms, but under certain conditions, the presence of light and nutrients can promote growth and reproduction. As a model organism was used unicellular alga *Desmodesmus subspicatus* (R. Chodat) E. Hegewald& A. Schmidt, strain SAG 86.01 from the Culture collection of cyanobacteria and algae from the Slovak Academy of the Science Growth and reproduction of the algae in the different kind of model media have identified inhibition or stimulation of the growth. The principle of the test was cultivation of *Desmodesmus subspicatus*- monospecific algal strain in the model defined media with nutrients and using of different types of physical impact (FAR solar radiation (400 –700nm), UV radiation (100 -280 nm). As the model media were used groundwater with different degrees of contamination, deionized water and the defined composition of drinking water. The initial biomass concentration in all tested samples was $4.3x10^3$ cell.ml^{-1}.
Duration of exposure was 72 hours by the temperature 30±1°C, the cell density was measured every 24 hours.During the test were the samples exposed by two different types of radiation: FAR ((Source - TL-D 36W/54-765 Philips (400 -700 nm)) and UV (Source -TUV UVC TL-D 36W G13 Philips (100-280 nm)). The concentration of biomass changing was evaluated in comparison to the biomass grown of the control cultures. The growth and cell viability was expressed depending on the concentration and the type and duration of radiation exposure. The different type of radiation in combination with sufficient nutrients in model water results in inhibition/stimulation of the growth of *Desmodesmus subspicatus*. The comparison of growth of the cultures with various media after irradiation FAR indicates growth stimulation in groundwater with the higher pollution (Fig. 1).
UV rays have a direct impact on photosynthesis. The lake is estimated this impact to a depth of 10-15 meters (Holzinger and Lutz 2006) .Thus as expected UV radiation caused the partial destruction of the cell wall (lipid peroxidation degradation of polysaccharides) which resulted in in inhibition of biomass (Mallick and Mohm 2000, Takáčová, 2013).For the successful elimination of the whole, grown biomass in technological treatment of water for human consumption, it is necessary to use an efficient process of radiation such as pipe system with a higher contact time - targeted photoreduction – ROS.

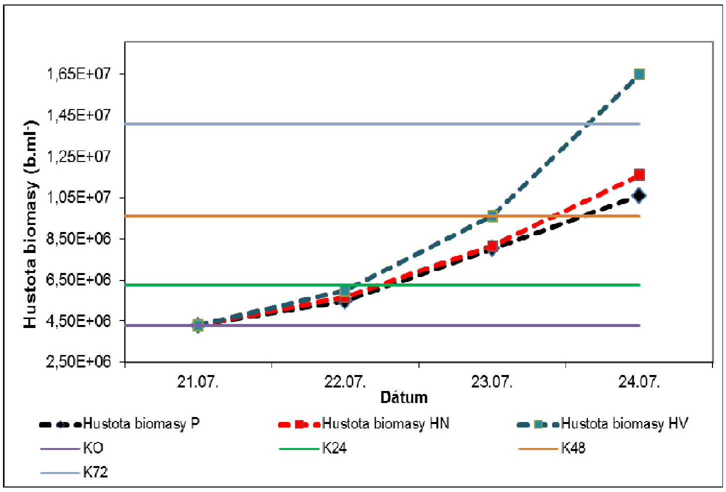

Fig. 1. Change of the concentration of algae biomass (*Desmodesmus subspicatus*) according to the aqueous matrix and durationof FAR radiation exposure.

A model species *Desmodesmus subspicatus* is known for its wide ecological valence. It is distributed in more than one temperature zone and is predetermined laboratory testing according to different requirements. Physical methods of hygienic treatment of water for human consumption in water supply are used in Slovakia. The current trend of ground water treatment represents a distribution to the consumer without disinfection.

The nutrient-enriched water can cause under certain conditions increasing of biomass, which can be a medium for secondary pathogenic microorganisms. Such a procedure is possible in groundwater are not influenced by surface water. When water is enriched by nutrients, it is possible under certain conditions, expected increase of the biomass, which can cause growth of the secondary pathogenic microorganisms. For this reason it is necessary to pay particular attention not only pathogenic and conditionally pathogenic microorganisms but also autotrophic, which are the creators of biomass and can become nutrients for decomposers and consumers.

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THE PHOTOACTIVE ZEOLITE COMPOSITE IN THE PROCESS OF WASTE REDUCTION

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ABSTRACT

Carbon capture and storage (CCS) only deals with the problem of reducing hazardous emissions of CO_2 in the atmosphere. The problem occurs when the storage space is filled. In this study, we used heterogeneous immobilized alga system - Fe-ZSM-Pt for capture of CO_2 in the chemical transformation of a compound of energy recoverable. The result of photodegradation effect of the prepared composites were different chemical compounds depending on the variability of conditions.

INTRODUCTION

Emissions of CO_2, mainly from the anthropogenic sources, cause serious impact on climate change. Thus the demand for active solution of these problems is still increasing. Existing methods of CO_2 capture are just partial solutions and generally problems take place in the next step. Therefore the essential question; what are we able to do with accumulated CO_2 can be raised. One possible way of CO_2 treatment is through the active solution in the form of photochemical reduction and subsequent conversion of CO_2 into organic products (e.g. source of alternative energy). Recycling has sense from the point of minimization of the next energy source demand, because just energy of photons is used. In our case, the modified zeolite Fe-ZSM5-PT via oxidative polymerization method was prepared, which is a photosensitive agent for photochemical reaction in the presence of UVA-VIS radiation. Zeolite matrix captures CO_2 thanks to hexagonal structure of ZSM5. Photoreduction then occurs in an anaerobic water environment in the presence of UVA-VIS radiation.

EXPERIMENTAL PART

The photochemical reduction of CO_2 in presence of modified zeolite Fe-ZSM-5-Pt

Lowering of CO_2 emission in the water environment through photo-catalytic processes can be also assigned among other recycling technologies. Useful organic compounds can be made as a part of renewable energy sources (de Richter a kol., 2013).
In our experiments, the photodegradation (UVA-VIS) of CO_2 with addition of modified Fe-ZSM5-Pt was used. The decrease of the concentration of CO_2 in reaction mixture and parallel increase of organically bonded carbon (TOC) caused by radiation (picture 1.) were observed.

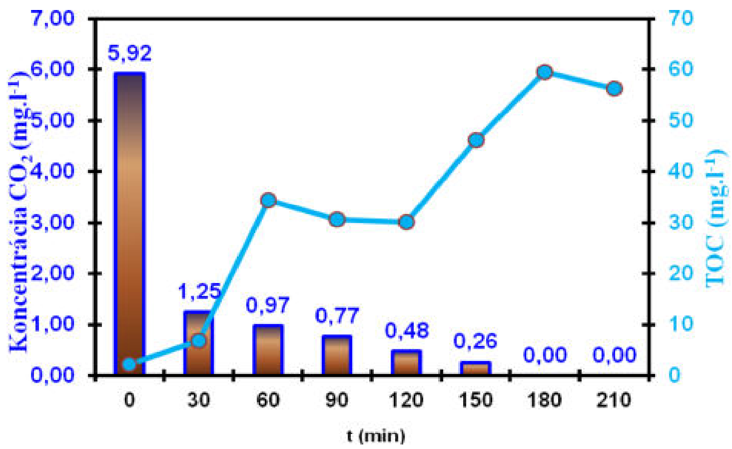

Fig. 1. Change of the concentration of CO_2 in solution (Fe-ZSM5-Pt, water, CO_2) exposed to UVA-VIS radiation in the closed system.

In the work of Čík et al. (1999) the forming of reactive oxygen by radiation of UVA-VIS on Fe-ZSM-5-Pt was observed.

$$PT + h\nu \rightarrow PT^{*} \rightarrow [PT^{\bullet +} + e^{-}] \xrightarrow{O_2(H_2O)} O_2^{\bullet -} \qquad k = 1{,}9.10^{10}\ dm^3.s^{-1} \qquad (1)$$

alebo

$$PT + h\nu \rightarrow PT^{*} \xrightarrow{O_2(H_2O)} [PT^{\delta +} \cdots {}^{1}O_2^{\delta -}] \rightarrow PT^{\bullet +} + O_2^{\bullet -} \qquad (2)$$

Consequently, the forming of hydrogen through decomposition of water during this reaction was also confirmed.

$$PT^{*} \xrightarrow{H_2O} PT^{\bullet +} + e^{-} \xrightarrow{H^{+}} H^{\bullet} \qquad k = 2{,}3.10^{10}\ dm^3.s^{-1} \qquad (3)$$

$$H^{\bullet} + H^{\bullet} \rightarrow H_2 \qquad k = 1{,}0.10^{10}\ dm^3.s^{-1} \qquad (4)$$

Analogously, the equations (3 and 4) Čík et al. (1999) can be also implemented for our reaction conditions as the same type of catalyst was used. Released hydrogen, forming as a gas phase during radiation can be seen in picture 2.

The reaction system was isolated, that means that exchange of substances with environment was none. The impact of radiation upon reaction component was done uniformly and only in the direction of one axis through water filter in order to prevent the overheating of system. In case of blank experiment made by deionized water the overheating of system was not observed. On the other hand, the overheating of reaction system was predominantly caused by chemical reaction. Reaction system was exposed to intense stirring in order to prevent the creation of concentration gradients.

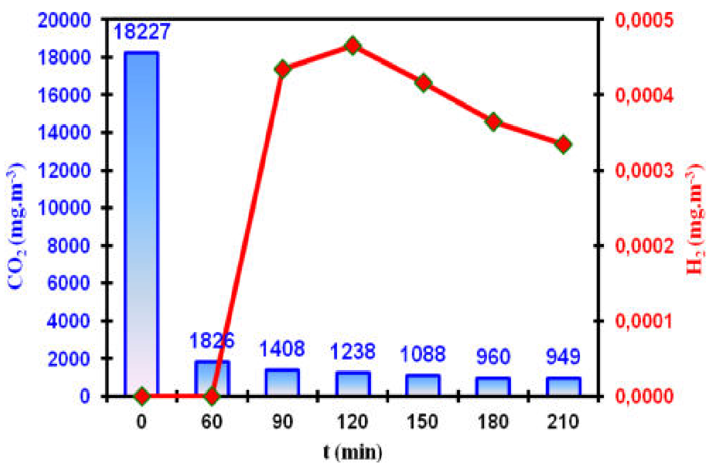

Fig. 2. The change of concentration of CO_2 and forming of H_2 in gas phase over reaction solution (Fe-ZSM-5-Pt, water and CO_2) exposed to UVA-VIS radiation in isolated system.

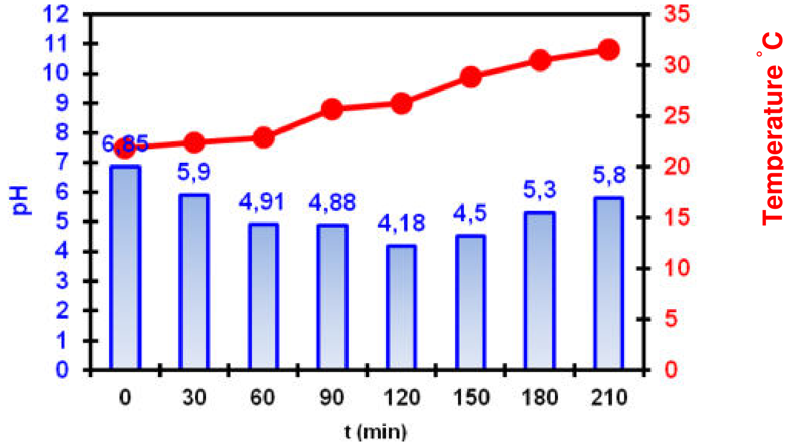

Fig. 3. The change of the CO_2 degradation conditions (pH, temperature) during radiation exposition in suspension (reaction system was made by 100ml of water with content of 300mg of modified zeolite Fe-ZSM-5-Pt and doped with CO_2 with concentration 5.92 $g.l^{-1}$).

Iron complexes presented in zeolite ZSM-5 (Fe-ZSM-5) reach remarkable redox activity. Heterogenic catalyst Fe-ZSM-5 was successfully used for selective oxidation of methane into methanol at room temperature in the presence of NO as oxidizer (Dubkov et al., 1997). High selective and active center of Fe-ZSM-5 is given by active iron atoms which are dispersed in complexes. Such complexes can be in the form of isolated ions, binuclear complexes in zeolite matrix (Battiston et al., 2003). The evolution of OH radicals was also mentioned by Čík et al. (2006), who worked with modified zeolite Fe-ZSM-5-Pt. During radiation caused by metal halogenide lamp (with intensity of radiation of 60W.m-2) at ambient temperature, following reactions can take place:

$$O_2 + e^- \rightarrow O_2^{\bullet -} \quad (5)$$

$$2\,O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet} \quad (6)$$

$$O_2^{\bullet -} + HO_2^{\bullet} + H^+ \rightarrow O_2 + H_2O_2 \quad (7)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (8)$$

$$H_2O_2 + e^- \rightarrow {}^{\bullet}OH + OH^- \quad (9)$$

$$H_2O_2 + H^{\bullet} \rightarrow {}^{\bullet}OH + H_2O \quad (10)$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow {}^{\bullet}OH + OH^- + O_2 \quad (11)$$

$$OH^- + PT^{\bullet +} \rightarrow {}^{\bullet}OH + PT \quad (12)$$

Created hydroxyl radicals enter into the reaction mechanism and attack soluble forms of CO_2 (e.g. HCO_3^- , CO_2) depending on the temperature and pH of the solution (picture 3). The possible theoretical mechanism of photoreduction of CO_2 onto modified zeolite Fe-ZSM-5-Pt is shown in picture 4.

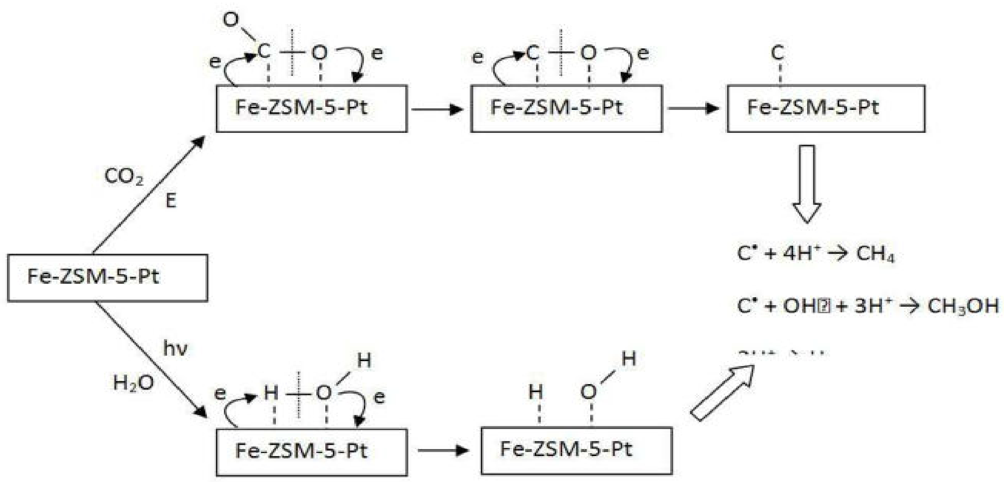

Fig. 4. Theoretical mechanism of photoreduction of CO_2 onto Fe-ZSM-5-Pt catalyst.

The possible evidence of this mechanism is EPR spectra of singlet oxygen by means of spin trap TEMP. The existence of singlet oxygen was increasing with higher exposure time as shown in picture 5.

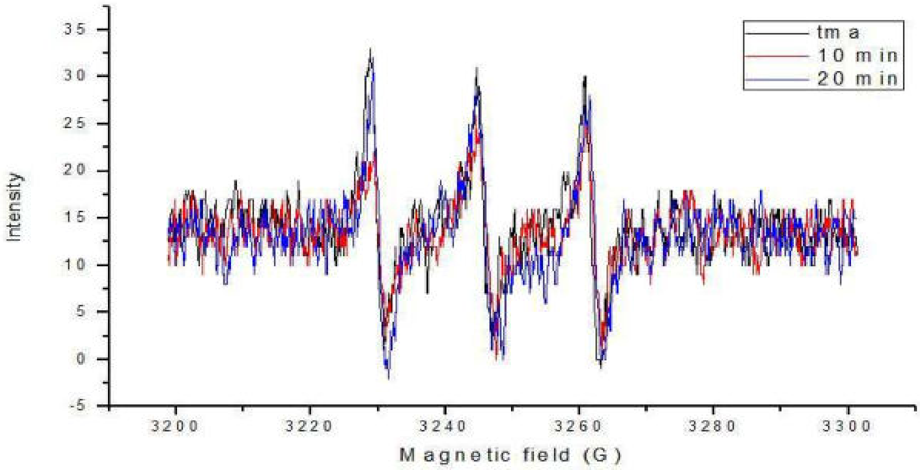

Fig. 5. The increase of singlet oxygen as a function of exposure time (CO_2, TEMPO-radicals trap, FE-ZSM-5-PT).

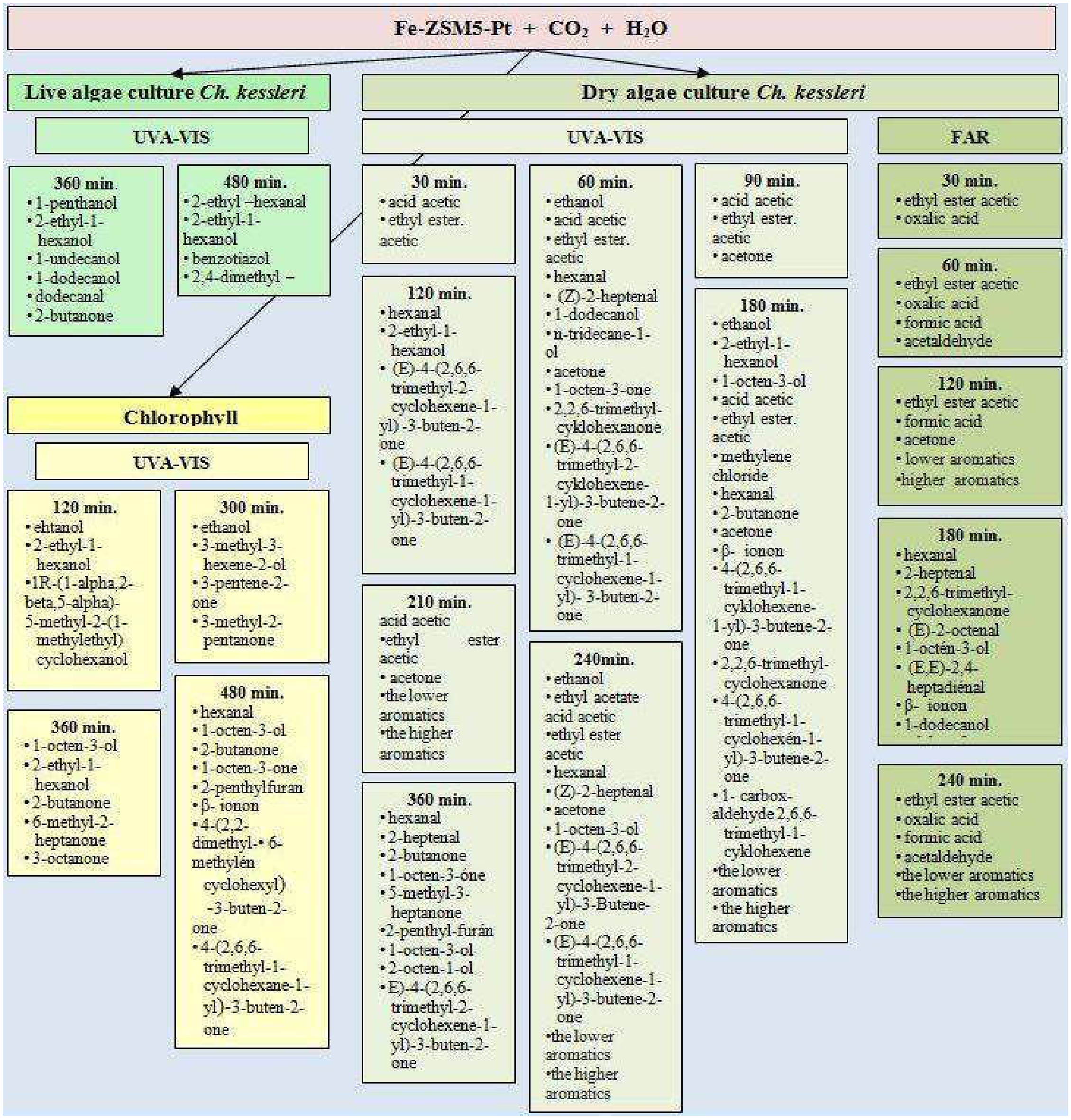

Fig. 6. Summary of identified products of photodegradation of CO_2 in heterogenic system Fe-ZSM-5-Pt and algae *Chlorella kessleri* or chlorophyll in the water environment.

CONCLUSION

The combination of zeolite matrix with biological system can offer considerable advantages. Inorganic host matrix enables immobilization of bio-component, which is the main condition for the usability in various applications (e.g. mechanical, chemical and photochemical stability). It can be assumed that the creation of such photo induced system is predicted in the creation of wide spectra of derived compounds. The addition of algae into heterogenic system was specifically aimed according to the presence of content ratio of active natural photosensitizer and chlorophyll a. Our assumption of intensified combined effect of algae immobilization on Fe-ZSM-5-Pt carrier was confirmed. The results obtained by the SPME-GC-MS technique for the algae culture were identified as products of photodegradation effect on cell membranes depending on the conditions of photodegradation of CO_2 in UVA-VIS radiation. In particular, there were higher alcohols (C10-C18) and esters of fatty acids (linoleic acid, palmitic acid). In case of combined photocatalyst Fe-ZSM5-Pt + dry algae culture, lower signals for ethanol were obtained. On the other hand, interesting results for ethanol were obtained in case of heterogenic system Fe-ZSM-5-PT + chlorophyll a.

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ALTERNATIVE PROCESSING OF ELECTRICAL WASTE

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KEYWORDS
Bioleaching, fungi, e-waste, aluminium

ABSTRACT

The aim of the paper was to investigate the efficiency of fungal strains applied in bioleaching of economically interesting metal - aluminium from e-waste. E-waste used in this study was composed from pulverized old computer printed circuit boards (PCB). For leaching experiments, three strains of the genera *Aspergillus* were used. Bioleaching was carried out as stationary systems at laboratory temperature for 28 days. Maximum mobilization of aluminium from e-waste was 62.36%.

World production of e-waste ranges from 30 to 50 million tons per year. Moreover, it increases annually for 3-5 % (Bas et al., 2013). Recycling of e-waste is important due to recovery of economically interesting metals such as aluminium, copper, iron, platinum, silverand gold as well as due to prevention of release and spreading out of toxic elements in the environment such as antimony, barium, cadmium, cobalt, chromium, lithium and mercury (Kiddee et al., 2013).At present, e-waste is processed by mechanical, hydrometallurgical and pyrometallurgical techniques. Disadvantages of these methods include high input and operating costs, production of huge amounts of toxic wastewater and release of harmful compounds in the atmosphere (Cui et al., 2008).The bioleaching with various microbial species could be a proper alternative for e-waste recovery. Advantages of such method include low input and operating costs and production of lower amounts of harmful wastewater(Wu et al., 2009).The aim of the study was to investigate the efficiency of applied strains of microscopic filamentous fungi originating from different types of the environment to recovery of aluminium from e-waste.

Aluminium occurs in PCB mainly in elemental form. For example, the concentration of aluminium in used e-waste was 8208 $mg.kg^{-1}$ (Tuncuk et al., 2012).Various authors investigating leaching of aluminium with organic acids from PCB found out that low pH values for efficient solubilisation of aluminium are required (Brandl et al., 2001; Kolenčík, 2013). The results in this study confirmed the necessity for using of low pH values for efficient aluminium extraction from PCB. Using the *A. niger* – Šobov fungal strain, the highest concentration of leached aluminium (63.36 %) was recorded (Tab. 1). This strain was able to change pH values to the lowest values from all applied fungal strains. The lowest pH value reached by this strain was 2.1 (Fig. 1). The strain was isolated from theDystricCambisol (contaminated and eroded)of former mine site of Šobov, Slovakia. The soil contains high contents of iron and aluminium. The second highest extraction efficiency was recorded with using the *A. niger* – ZemianskeKostoľany strain reaching 13.44 % (Tab. 1).Lower leaching efficiency was caused by higher pH value during bioleaching (Fig. 1). The *A. niger* – Zemianske Kostoľany strain was isolated from technosol containing brown-coal derived ashes in the Zemianske Kostoľany site. The substrate contains high contents of arsenic. The lowest efficiency of aluminium mobilization (9.2 %) was recorded during bioleaching with the *A. niger* – Gabčíkovo strain (Tab. 1). The strain was isolated from the flooded forest soil in the Gabčíkovo site. No toxic elements were determined in the soil and pH value ranged 7.7.

Tab.1. Efficiency of aluminium extraction fromcomputer printed circuit boards after bioleaching by *Aspergillusniger* strains

Strains used in bioleaching	Efficiency of aluminiumextraction
***Aspergillus niger*- Šobov**	62.36%
***Aspergillus niger*-ZemianskéKostoľany**	13.44%
***Aspergillus niger*- Gabčíkovo**	9.2%

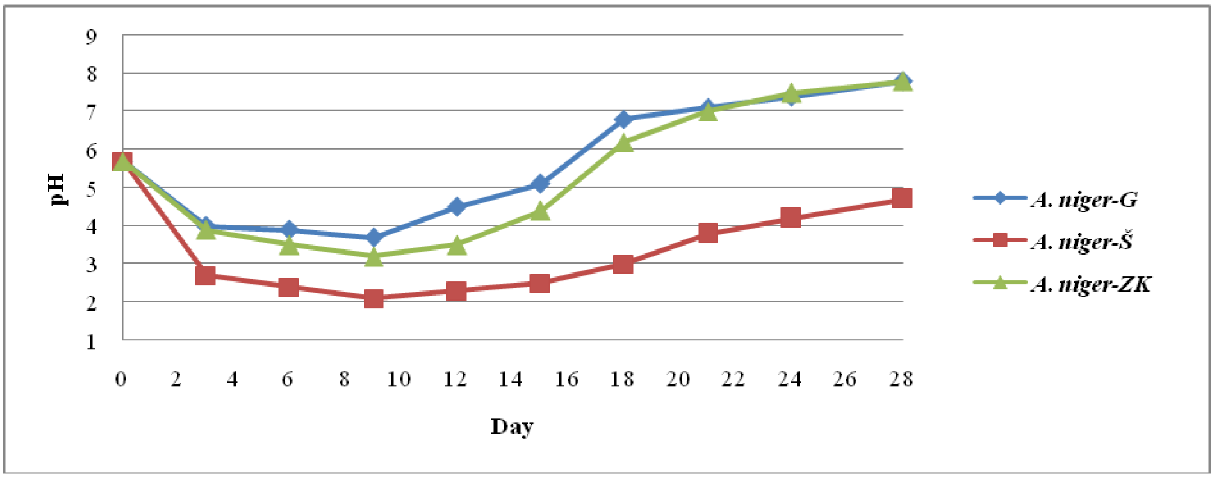

Fig. 1. Changes in pH evolution duringbioleaching ofcomputer printed circuit boards with*Aspergillusniger* strains

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SOIL CONTAMINATION IN THE URBAN AREA IN SERBIA

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KEYWORDS
Contaminated sites, urban soils, heavy metals, contamination level, risk assessment

ABSTRACT

In the territory of Serbia 394 potentially contaminated and contaminated sites have been identified near urban areas. From a total number of sites, 189 belongs to industry, while 181 are municipal waste disposal sites. The presence of heavy metals in urban soils is one of the most common environmental contamination problem usually caused by industrial discharges. Systematic examination of urban soils in Serbia has been done since 1999 to determine the contamination level and potential risk to population health. This paper reports on urban soil contamination near municipal waste sites and industrial facilities in the period 2010-2015. The research was done in eleven cities and nine municipalities. The analysis shows that the degradation of urban soils can be attributed to many factors including: the impacts of urbanization and industrialization, unsupervised communal waste sites, partially uncontrolled agro-chemical practices and low levels of communal hygiene. The results of analysis for 200 samples show that in the majority of samples the prescribed limit values for Cd, Pb, Cu, Zn, Ni, Cr, Co, As and Hg are exceeded. Intervention values are exceeded in a small number of samples for Cu, Zn, Ni, Cr and As. The implementation of environmental protection measures is only possible when stimulated by scientific-technological research carried out in this field.

INTRODUCTION

Due to a rapid urbanization, most of the urban areas in Serbia are built close to roads or industrial areas, where they are under the impact of pollution sources such as industrial emissions. The current knowledge of the pollution of urban soils was reviewed with special reference to heavy metals and this study has demonstrated a serious problem of heavy metal contamination in urban areas.

RESULTS AND DISCUSSION

An important aspect of soil contamination is the level to which the contaminants are present in the soil and those concentrations are expressed in units of the mass of heavy metal per units of the mass of soil (mg/kg). [1] Samples were collected from 0-30 cm depth.The 99 samples are collected nearmunicipal waste sites and the rest of 101 samples are collected near industrial facilitieson the territory of Serbia (Figure 1). Percentage of samples that have exceeded the prescribed limit values for 9 heavy metals are presented onFigure 2.

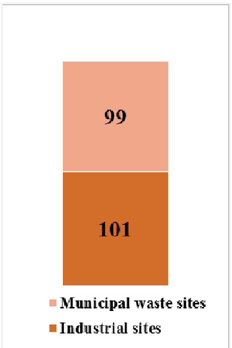

Fig. 1. The total number of samples

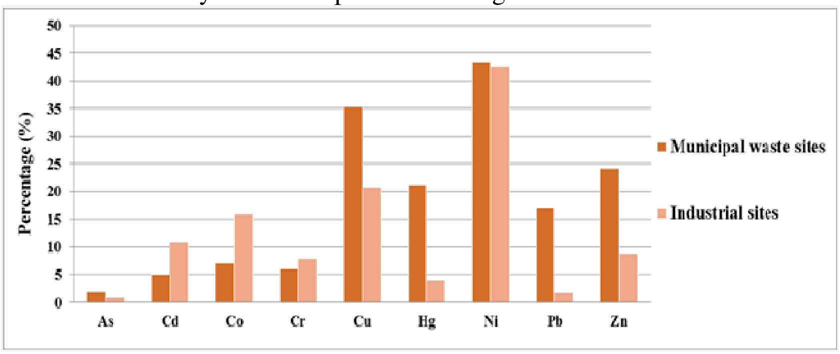

Fig. 2. Percentage of samples exceeding the limit values

The high concentration of nickel found in samples is believed to be of geogenic origin, which is specific for Western Serbia. [4] Results of soil analysis show big differences between samples collected near municipal waste sites and industrial sites. According to the results of exceeding limit values, near municipal waste sites Cu, Hg, Pb, and Zn were found in greater number of samples, while Cd, Co, and Cr near industrial sites.[1]

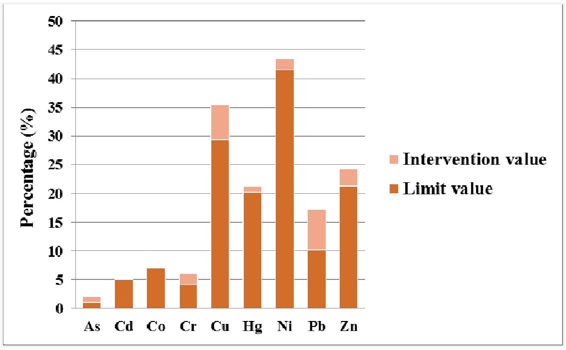

Fig. 3. Percentage of samples exceeded prescribed values collected near municipal waste sites

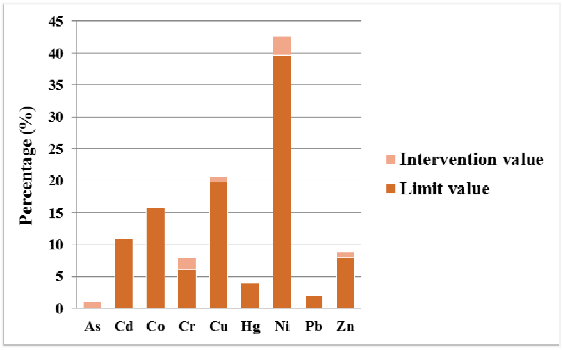

Fig. 4. Percentage of samples exceeded prescribed values collected near industrial sites

The intervention values for soil remediation indicate when the functional properties of the soil for humans, plants, and animals is seriously impaired or is in danger of being so. They are representative of the level of contamination above which a case of soil contamination is deemed to be severe.Samples collected near municipal waste sites exceeded intervention values for As, Cr, Cu, Hg, Ni, Pb, and Zn (Figure 3), while near industrial sites, intervention values are exceeded for As, Cr, Cu, Ni, Zn (Figure 4). [1] The highest percentage of exceeding intervention values were found in samples collected near municipal waste sites. Of the total number of samples that have exceeded the limit values for lead in soils near municipal waste sites, even 40% of the samples exceeded the intervention values.


Fig. 5. Waste disposal sites in Western Serbia (photo: Serbian Environmental Protection Agency)

CONCLUSION

The dominant contaminants in the analyzed urban soils near municipal waste sites are Cu, Hg, Ni, Pb, Zn, while Cd, Co, Cu and Ni are dominant in soils near industrial sites.Results of this study show a bit better status of urban soils near industrial sites. A possible explanation lies in the fact that open dumping and landfilling have represented the predominant method of waste management in Serbia during the past decades. This practice resulted in over 3085 illegal waste disposal sites distributed all over the country.[5] 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.[3] According to the State of the Environment Report for 2014, on the territory of Serbia has so far built seven sanitary landfills, and two are in the process of obtaining permits, which we consider as a progress in waste management practice.[5]A multidisciplinary approach in the assessment of contaminated urban sites is needed to ensure that urban soils are well understood. The implementation of environmental protection measures is only possible when stimulated by scientific-technological research carried out in this field.[2] Contamination of urban soils is our immediate concern relating to potential impact on human health. The health risks of exposure to urban soil contaminants such as heavy metals have not been yet observed and documented. Further analysis ofsoils in urban areas is needed to assess the potential impact on environmental media and human health.

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CADMIUM IN SOILS OF BOSNIA AND HERZEGOVINA

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KEYWORDS
Total content of cadmium, maximally allowable concentration, Bosnia and Herzegovina

ABSTRACT

Use of soil is in practice carried out in multifunctional manner, in other words, from the aspect of its ecological and technical functions. These two basic groups have tendencies for the same land area so the question emerges whether it is possible to harmonize relationship between two of them. As a result of use of soil from the aspect of its technical functions, soil suffers great consequences which vary from temporary exclusion from crop production to its permanent destruction.
Among the many damages to soil, contamination of soil with heavy metals draws the most attention. The distribution of heavy metals in the soil, their mobility and solubility depends on the standdard properties of soil (soil reaction, content of colloidal particles in the soil clay content, the content of organic matter of soil). Heavy metals in the soil do not dissolve like many other pollutants, so the decontamination of soil is by rule a long-term process with great investments that lasts even for decades.
Contaminated surfaces of about 750 ha. In the studied soils were taken average samples at depths of 0-20 cm.Extraction of traces of total content of heavy metals (BAS ISO 11047: 2000, AAnalyst 800, Perkin Elmer (2006), software, WinLab32, version 6.4. Rev. 6).
In all tested samples the content of total cadmium (Cd) is below the maximally allowable concentration (MAC) and far below remediation value. When it comes to the corrected limit value, the content of total cadmium is below this value only in mullock dumps.
In order to take measures to reduce the concentration of heavy metals in the soil, and through it in plants, it is necessary to accurately determine the source of pollution and therefore take measures to protect agricultural land compliant with the requirements of national legislation. Therefore, it is very important regular analysis of farmland, particularly beside large industrial plants, settlements and roads, taking measures for its alleviation, among other things, proper selection of plant species and genotypes that are more tolerant to increased concentrations of toxic elements in the air and land.

INTRODUCTION

Use of soil is in practice carried out in multifunctional manner, in other words, from the aspect of its ecological and technical functions. These two basic groups have tendencies for the same land area so the question emerges whether it is possible to harmonize relationship between two of them. As a result of use of soil from the aspect of its technical functions, soil suffers great consequences which vary from temporary exclusion from crop production to its permanent destruction(Kraisniket al. 2012).
Republic of Srpska has about 0.85 ha of agricultural soil per capita, of which about 0.60 ha is arable (ploughland, gardens, orchards, vineyards, meadows) i.e. about 0.40 ha of ploughland and gardens. Currently, only about 0.20 ha per capita is cultivated. The above data show that the degree of utilization of the natural resources in Republic of Srpska is low with a trend of reduction. Throughout the world, the surface of 0.10 ha of arable land per capita is considered the lower limit (Agricultural Development Strategy of Republic of Srpska until 2015). Annual losses of soil, in Republic of Srpska, in the process of its destruction, amount to more than 1,500 hectares (Nature Protection Strategy of Republic of Srpska). In Bosnia and Herzegovina, according to NEAP's data for 2003, 900 ha disappears in open pits and 300 ha in dumps annually.
Among the many damages to soil, contamination of soil with heavy metals draws the most attention. The distribution of heavy metals in the soil, their mobility and solubility depends on the standdard properties of soil (soil reaction, content of colloidal particles in the soil clay content, the content of organic matter of soil). Heavy metals in the soil do not dissolve like many other pollutants, so the decontamination of soil is by rule a long-term process with great investments that lasts even for decades Tunguz et al. (2014).

MATERIALS AND METHODS

In the area of Gacko plain there was a disturbance of the land and to its destruction due to changes in land use, or permanent loss of land due to the construction of thermal power plants. Contaminated surfaces of about 750 ha. In the studied soils were taken average samples at depths of 0-20 cm.
Soil samples in undisturbed condition were taken from individual genetic horizons, in three repetitions, by cylinders of Kopecký.Extraction of traces of total content of heavy metals (BAS ISO 11047: 2000, AAnalyst 800, Perkin Elmer (2006), software, WinLab32, version 6.4. Rev. 6).

RESULTS AND DISCUSSION

The surveys covered limestone-dolomite soils, soils of dumps in the process of re-cultivation and mullock dumps.
FBiH legislation that was used according to the Law on Agricultural Soil (Official Gazette of FBiH, no. 52/09) i.e. Instructions on determining the allowable amount of harmful and dangerous substances in soil and methods for their investigation (Official Gazette of FBiH, no. 72/09) treats pollution i.e. contamination of soil by heavy metals in terms of growing the crop plants, i.e. as agricultural soil, based on textural characteristics.
If the concentration of heavy metals in the soil is significantly higher than normal, it indicates contamination either from anthropogenic sources or their natural geochemical origin. Control of their levels in the soils occurs through comparisons with maksimally allowableconcentration (MAC) for unpolluted soils.
In Serbia, the criteria for the assessment of soil contamination with heavy metals (MAC) are given in the Regulations on permitted amounts of dangerousand harmful substances in soil and water for irrigation and methods for their investigation (Official Gazette of RS, no. 23/94) and the Regulation on the program for systematic monitoring of soil quality, indicators for risk assessment of soil degradation and methodology for development of remediation programs (Official Gazette of RS, no. 88/2010).
The limit values for the maximally allowable concentration (MAC) of heavy metals in soils represent a significant foothold in the assessment of soil contamination by these mainly toxic elements.
Limit values, remediation values are valuethat can point to significant contamination for heavy metals in this case camdium (Cd) and depend on the clay content and/or organic matter in the soil. Data on the total content of cadmium (Cd) are shown in Tab. 1.

Tab.1. Mean values of the total content of cadmium (Cd), mg/kg, corrected limit values and remediation values for all soil types, soils of dumps in the process of re-cultivation and mullock dumps

Soils and dumps	Cadmium (Cd)	Corrected limit value (mg/kg)	Remediation value (mg/kg)
Soils	1.28	0.77	11.52
Soils of dumps in the process of re-cultivation	1.85	0.66	9.96
Mullock dumps	0.40	0.62	9.36

The maximally allowable amount of cadmium (Cd) in the soil is 3 mg/kg (Official Gazette of RS, no. 88/2010; Scheffer and Schachtschabel, 1998). The average content of cadmium in soils of Central Serbia is 0.805 mg/kg (Report on the state of soil in the Republic of Serbia, 2009).It is believed that in addition to geochemical origin Cd is often found in soils rich in Zn ore, carbonates, phosphorites, black shales and clays.

CONCLUSION

In all tested samples the content of total cadmium (Cd) is below the maximally allowable concentration (MAC) and far below remediation value. When it comes to the corrected limit value, the content of total cadmium is below this value only in mullock dumps.
In order to take measures to reduce the concentration of heavy metals in the soil, and through it in plants, it is necessary to accurately determine the source of pollution and therefore take measures to protect agricultural land compliant with the requirements of national legislation. Therefore, it is very important regular analysis of farmland, particularly beside large industrial plants, settlements and roads, taking measures for its alleviation, among other things, proper selection of plant species and genotypes that are more tolerant to increased concentrations of toxic elements in the air and land.

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HEAVY METAL CONTAMINATION OF THE ALLUVIAL SOILS OF THE MIDDLE NILE DELTA OF EGYPT

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KEYWORDS
Soil contamination, X-ray fluorescence spectrometry, remote sensing, Geographical Information Systems, the inverse distance weighted (IDW), Middle Nile Delta, Egypt.

Areas contaminated by heavy metals were identified in El-Gharbia Governorate (District) of Egypt. The study area occupies the Middle part of the Nile Delta of Egypt (30°45´20″ - 31°10´50″ E; 30°35´10″ - 31°10´05″ N; altitude 0-12 m above sea-level). The soil temperature regime of the study area is Thermic and the soil moisture regime is Torric. Sediments were mainly deposited in the Upper Pleistocene, which is evidenced by the deposits of the Neonile, which are mainly composed of medium and fine silts. Heavy metal analysis used several techniques, including remote sensing and Geographical Information Systems (GIS) as the main research tools. Digital Elevation Models (DEM), Landsat 8 and contour maps were used to map physiographic units.

Satellite images show that the study area is a flood-plain and includes high terraces (12.04% of area), moderately high terraces (22.41%), low terraces (21.67%), high decantation basins (2.05%), low decantation basins (12.26%), high overflow basins (12.68%), low overflow basins (10.71%), riverlevees (5.38%) and swales (0.77%). Thirty soil profiles were sampled in different physiographic units in the study area. Geochemical analysis of the 110 soil profiles samples was conducted using X-ray fluorescence spectrometry (XRF). Vanadium (V), nickel (Ni), chromium (Cr), copper (Cu) and zinc (Zn) concentrations were measured. V, Ni and Cr concentrations exceeded recommended human health safety valuesin all horizons of the soil profiles, while Cu had a variable distribution. Most Zn concentrations were under recommended concentration limits. Heavy metal risk was calculated using the Contamination factor (CF). CF was variable and suggests that soilsin the study area ranged from low contamination to very high contamination classes in terms of the analysed metals. The spatial interpolation method (IDW) was used with 12 neighbouring samples for estimation of each grid point. A power of two was used to weight the nearest points. In terms of the distribution of heavy metals in the different physiographic units, the swales unit contained the highest concentration, as this is in Kfr El Zayat, which has many factories. V, Cr, Ni, Cu and Zn concentrations are significantly inter-correlated. There are no significant correlations between major elements and heavy metal concentrations, except for V, Ni and Zn. V and Ni have significant positive medium and strong correlations with Fe, respectively. According to the analysis of major elements, these deltaic soils are predominantly siliceous, with slight enrichment of the alumina component.

We recommend that heavy metal contamination be studied within entire soil profiles and not just top-soils; because these metals affect soil and crop quality and can cause ground-water pollution. Protection against this hazard is vital for sustainable land management. Precise measures and efficient methods to improve soil and water quality must be conducted, in order to prevent soil and water pollution and to avoid the need for costly remediation in the future.