INTERNATIONAL CONFERENCE
CONTAMINATED SITES
BRATISLAVA 27–29 MAY 2015

INTERNATIONAL CONFERENCE

CONTAMINATED SITES BRATISLAVA 2015

CONFERENCE PROCEEDINGS

European Union

SLOVENSKÁ AGENTÚRA
ŽIVOTNÉHO PROSTREDIA

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CONTAMINATED SITES BRATISLAVA 2015

Ministerstvo životného prostredia Slovenskej republiky   op | žp   EURÓPSKA ÚNIA

27 –29 MAY, 2015

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THE POSSIBILITIES OF USING EUROPEAN FUNDS TO ADDRESS THE CONTAMINATED SITES IN SLOVAKIA

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INTRODUCTION

Contaminated sites in Slovakia represent a serious problem, the solution of which was successfully started in 2006, when the nationwide project "Systematic Identification of Contaminated Sites in the Slovak Republic" was implemented. Thanks to this project there were about 1,800 sites identified, which were contaminated by various chemicals as a result of long-term human activities. About 1200 of them poses a risk to human health and the environment. Based on the results of the project the Information system of contaminated sites was built in 2008. In 2010 the State Remediation Programme of Contaminated Sites was approved by the Slovak government. The one thing missing relative to this issue was a comprehensive legislative framework and enactment of the polluter pays principle. Gradual steps led to the revision of the Geological Act in 2009 – Act no. 569/2007 Coll. on Geological Works (Geological Act) and the Regulation of the MoESR no. 51/2008 implementing the Geological Act. In 2011, the Ministry of the Environment of the Slovak Republic was successful in enforcing the law on "Contaminated Sites", Act no. 409/2011 Coll. The preparation of amendments of some acts took almost eight years. After these significant steps in the field of contaminated sites, appropriate conditions had finally been set that enabled the use of European funds through the Operational Programme Environment (2007–2013) and the Operational Programme Quality of the Environment (2014–2020).

LEGISLATIVE FRAMEWORK

Addressing contaminated sites in Slovakia is regulated by two legal regulations - the Act no. 409/2011 Coll. on Certain Measures in Relation to Contaminated Sites and the Act no. 569/2007 Coll. on Geological Works (Geological Act). The Act on contaminated sites regulates the identification and classification of contaminated sites, defines producer, provision for the determination of the person liable for the contaminated sites and his obligations, establishes a procedure when a liable person cannot be identified, defines work plan for the remediation of contaminated sites and the bodies of state administration in the field of contaminated sites. The Geological Act regulates, inter alia, some of the definitions in the field of contaminated sites, responsibilities and competencies necessary for the performance of geological works (which are primarily investigation, monitoring and remediation of contaminated sites), designing geological projects, their implementation, required documentation, final reports, approving those reports and their transfer to the archives. It also provides conditions of access to land and restriction of property rights, which in many cases represents a serious problem for a contractor of geological works. In March 2015 came into force an amendment to Decree no. 51/2008 Coll. implementing the Geological Act. In relation to contaminated sites the Decree amends several provisions. For example, it defines the roles of professional geological supervision, specifies stages of hydrogeological survey, requirements for the design of geological projects and final reports. In February 2015 came into force the Directive of the Ministry of Environment of the Slovak Republic no. 1/2015 -7. on risk assessment of contaminated sites.

The Directive lays down general principles for risk analysis of contaminated sites, the basic content and method of its preparation. It also regulates the procedure for evaluating data on the examined area, risk identification, environmental risk assessment, health risk assessment and setting targets for the remediation measures.

STATE REMEDIATION PROGRAMME OF CONTAMINATED SITES

The State Remediation Programme of Contaminated Sites is a basic strategic and planning document for issues of contaminated sites in Slovakia. According to provision § 20a of the Geological Act, it is primarily drafted and maintained by the Ministry of the Environment on the basis of data from the Information system of Contaminated sites. The current State Remediation Programme of Contaminated Sites for the period 2010–2015 was approved by the government of the Slovak Republic in March 2010 and it is available on the website of the Ministry of the Environment or at www.vlada.gov.sk. Due to the expiration of validity, the Ministry of the

Environment in cooperation with the Slovak environmental agency prepare proposal of a new State Remediation Programme of Contaminated Sites for the years 2016 - 2021, which will be decisive for the use of EU funds.

OPERATIONAL PROGRAMME ENVIRONMENT (2007-2013)

The Operational Programme Environment (2007 - 2013) includes contaminated sites under the operation axis 4. Waste and under Operational objective 4.4 Addressing contaminated sites including their removal. There are defined the following eligible groups of activities:

- Group I: Monitoring and investigation of contaminated sites and processing of risk analysis,
- Group II: Remediation of contaminated sites,
- Group III: Completing information system of contaminated sites.

Group I: Monitoring and investigation of contaminated sites and processing of risk analysis is focused on the following types of projects:

A. Projects of risk analysis, feasibility studies, remediation projects, remediation programmes and audits of contaminated sites,
B. Projects of investigation of potentially contaminated sites,
C. Projects of detailed and additional investigation of the most risky contaminated sites,
D. Regional studies of contaminated sites impact assessment on the environment,
E. Projects of monitoring systems building of the most risky contaminated sites.

Group II:Remediation of contaminated sites is focused on:

A. Projects of remediation of contaminated sites representing a high risk to human health and the environment.

Group III: Completing of information system of contaminated sites is aimed on:

A. Project of completion of the information system of contaminated sites as part of the public administration information system,
B. Project of development of the Atlas of remediation methods as part of the information system of contaminated sites,
C. Projects focusing on public relations, education and promotion activities concerning the remediation of contaminated sites.

Within the calls for applications for grants has been so far supported several projects, the most important are:

- Regional studies of contaminated sites impact assessment on the environment in the selected regions,
- Atlas of remediation methods of contaminated sites,
- Education, public relations as support in addressing contaminated sites in Slovakia,
- Completion of the information system of contaminated sites,
- Investigation of contaminated sites in selected localities of the Slovak Republic (54 sites),
- Monitoring of contaminated sites in selected localities of the Slovak Republic (161 sites),
- Remediation of contaminated site in the Quarry Srdce,
- Remediation of contaminated sites in selected localities of the Trencin region (2 sites),
- Remediation of contaminated sites in selected localities of the Trnava region (2 sites),
- Remediation of contaminated sites in selected localities of the Banska Bystrica region (2 sites),
- Remediation of contaminated sites in selected localities of the Nitra region (3 sites),
- Remediation of contaminates sites in selected localities of the Prešov and Košice regions (3 sites),
- Remediation of contaminated sites in selected military localities (6 sites - Lešť – garages, Lešť - the main camp, Ivachnová, Rimavská Sobota, Sliač, Nemšová).
- Potentially contaminated sites – investigation of selected localities of the Slovak Republic (87 sites);

- Integration of the public in dealing with contaminated sites.

Two projects submitted under the last call are currently being adopted:

- Geological investigation of potentially contaminated through remote sensing and modelling,
- State Remediation Programme of Contaminated sites (2016 – 2021).

OPERATIONAL PROGRAMME QUALITY OF THE ENVIRONMENT (2014 - 2020)

The main objective of the Operational Programme Quality of the Environment is to promote the sustainable and efficient use of natural resources, ensuring environmental protection, active adaptation to climate change and promote energy efficiency and low carbon economy. In order to achieve this overall objective the investment strategy of the operational program including three basic thematic objectives has been proposed to:

1. Support the transition to a low-carbon economy in all sectors,
2. Support for climate change adaptation, risk prevention and risk management,
3. Protect environment and promote resource efficiency.

The Ministry of the Environment will act in accordance with the document „Proposed structure of the operational programs for the multiannual financial framework of the European structural and investment funds for the programming period 2014 – 2020“ as the managing authority.

Promoting the sustainable use of natural resources through environmental infrastructure development will be implemented within the Operational Programme Quality of the Environment through number of investment priorities. The Investment Priority 4 of the Priority Axis 1 is focused on „Taking measures to improve the urban environment, urban regeneration, recovery and decontamination of brownfield sites (including areas undergoing change)“. The aim of this investment priority is to increase the share of remediated sites that represent at present a constant risk on human health and the environment.

The specific objectives will be met through the following activities:

A Investigation, remediation and monitoring of contaminated sites in urban environment and in brownfield sites (including areas undergoing change),

B. Improving the awareness of issues of contaminated sites.

The proposed activities will build on previously completed investigation and monitoring projects of contaminated sites. It will be necessary to perform many tasks, such as:

a) Constant updating of the information system of contaminated sites,
b) Investigation of priority contaminated sites, including elaboration of risk analysis of polluted areas,
c) In the case of extensive contamination to ensure elaboration of feasibility studies of remediation of contaminated sites,
d) Remediation of contaminated sites in accordance with the "polluter pays principle" and in accordance with the rules on state aid,
e) Monitoring of contaminated sites.

The activities improving the public awareness of issues of contaminated sites will be directly linked to activities of exploration, remediation and monitoring of contaminated sites.

CONCLUSION

The year 2015 is extremely difficult for the entities using the funds of the European Union. From the perspective of the Ministry of the Environment all projects financed from the Operational Programme Environment have to be completed by the end of this year and the most efficient utilization of allocated funds have to be ensured. On the other hand, it is necessary to prepare programming documents for the new Operational Programme Quality of the Environment, to boot first calls and to prepare applications for grants. The good news is that more than 4.3 billion € has been allocated for the Operational Programme Quality of the Environment, which represents the highest amount among all operational programs in Slovakia.

25 YEARS CONTAMINATED SITES REMEDIATION IN AUSTRIA – SUCCESSES, EXPERIENCES AND CHALLENGES

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KEYWORDS

Soil and water policy, site remediation

ABSTRACT

In 1989 Austria amended its environmental legislation and started a national program for registering, investigating and funding the remediation of historically contaminated sites causing serious environmental or human health risks. Since a national priority list is updated twice a year. Among 212 remediation projects at 135 sites, which have been initialized so far, the most hazardous and urgent sites have already been remediated. The total of public funding during this time amounted up to more than 1 billion EURO. As a complementary action the national inventory has been finalized by 2013 and 68.000 sites are registered within a database. The identification process for the national investigation program is ongoing and shall be completely established until 2025, the remediation program until 2050. A major revision and transition of the existing legal framework is under discussion since 2012. With regard to investigation, assessment and remediation the presentation will highlight successes and experiences during the last 25 years and explore future directions in managing historically contaminated land (soil and groundwater).

GROUNDWATER AND SOIL PROTECTION – GENERAL POLICY OBJECTIVES

Since an amendment to its constitution in 1984 the Republic of Austria is committed to comprehensively protect soil and water resourcesfor maintaining a place worth living for its citizens.This common responsibility to protect our environment asks for complementary efforts, which also touch on historically contaminated sites. Abandoned landfills and former industrial sites still can cause environmental contamination being of high local public interest. Therefore site remediation and developing tailored management strategies stays being an important pillar of environmental protection in practice and at a policy level as well.

Besides contamination Austria faces major environmental challenges by land –take, as by new buildingsand infrastructure projectsthe lossof fertile soils has increased to 22 ha per day.Given this trend holds on, it will takeonly200 years to bury productive soils and loose agricultural production completely.Furthermore due to neglecting soil functions and depleting ecosystem services like storage and retention of water by soils, increasing damages caused natural hazards like flooding are already to be observed.Therefore discussions on future policy objectives are shifting towards an integrated land management for balancing ecosystem services regionally. Management and reuse of historically contaminated sites and brownfield rehabilitation shall be one of the means for decreasing pressures in soil and water resources. Referring to European policy targets e.g. defined through the “Roadmap on Resource Efficiency” (2011) contaminated site remediation needs to support nature protection and contribute to the long-term target of having no net land-take by 2050.

CONTAMINATED SITE MANAGEMENT– LEGAL AND INSTITUTIONAL FRAMING

The general legislative background for contaminated sites refers in Austria to water protection (WRG 1959), the Industrial Code (GeWO, 1973) and waste management (AWG, 1990). In particular water protection and waste management schemes are based on a precautionary approach and therefore rather strict.

In 1989 legislation with regard to historically contaminated sites (ALSAG, 1989) has been enacted and established a public fund to finance remediation This was an important stepcomplementingenvironmental policy, which became an effective tool in international comparison as well. The law has several key aspects, among which a new waste tax to finance investigation and remediation projects,striving for a systematic identification of abandoned landfills and industrial sites, and a competence to coordinate and concentrate legal responsibilities were most important.As a resultthe national programme in Austria realised more than 1.400

millionEURO over a time period of 25 years. Up to 15 % of the budget may be used for data collection and investigation, whereas 85 % are dedicated to finance remediation. Environment Agency Austria is the main player for identification, investigation, assessment, prioritization and the data collection.Given a site owner or the legal successor is not liable for pollution, there is the opportunity to apply for public funding. The fund is managed by KPC (Kommunalkredit Public Consulting GmbH; see www.publicconsulting.at). Asat several seriously contaminated sites activities already had been ceased completely and no interested parties acted, the Austrian Environment Ministry funded in 2004 a private company (BALSA; see www.balsa-gmbh.at) being responsible for remediation at such "orphan" sites.

THE AUSTRIAN REMEDIATION PROGRAMMEDURING THE LAST 25 YEARS – AN OVERVIEW

Starting around 1960 a continuous industrial and commercial development took place in Austria generating general welfare to citizens. As one of the unintended environmental consequences groundwater contamination at several landfills became evident in the beginning of the 1980ies. The identification of a regional contaminationand a landfill ("Fischerdeponie") impacting groundwater resources in a region south of Vienna caused a big scandal and headlines in newspapers, making the general public sensible with regard to landfills and industrial legacies. As a consequence waste management policies changed, sequentially landfills were closed, a national groundwater monitoring programme has been initiated, the national programme on remediating historically contaminated sites was launched (see next chapter) and remediation of such point source pollution started.

Fig. 1."Fischerdeponie" after remediation - aerial photo (source: BALSA GmbH; www.balsa-gmbh.at)

In the 1990ies several investigations had been done but also remediation projects started. The remediation projects during this decade focused on landfill remediation. Therefore mostly digging out the contamination or containment by slurry walls were the solution. In general this was usually done in combination to pump-and-treat-systemsto stop and control groundwater contamination. Until 2000 the focus started to changefrom landfills towardsindustrially contaminated sites.

Thus result of25 years investigating, assessing and remediating historically contaminated sites can be summarised as follows:

- By 2013the national inventory has been completed (> 95 %) and 5000 landfills and 63.000former commercially or industrially used sites are registered.

- To characterise these sites the database includes basic data (e.g. contaminants, hydrogeology, land use) and is combined to a geographical information system.
- For some thousandsdata from field investigation are available or under processing.Due to a preliminary assessment the probability of severe environmental risks hasbeen classified as unlikelyat approximately 2.500 sites.
- At 277 serious environmental contamination or risks have been identified and prioritised with regard to public funding within the national remediation programme.
- Already 141 landfills and industrial sites have been remediated and therefore delisted.Currently 65 landfills and industrial sites are registered without a remediation project. At further 71 sites a remediation project is either ongoing or planned.

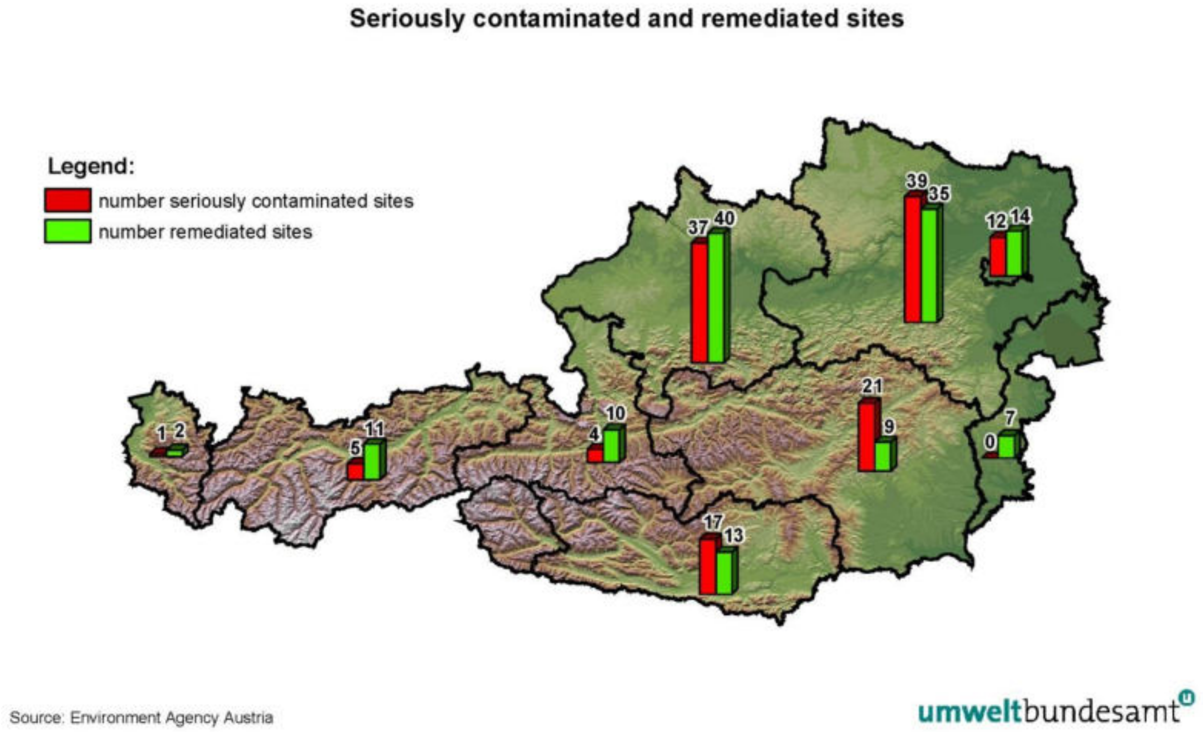

Fig. 2. Seriously contaminated sites and remediated sites in Austria (by January 1st, 2015) - number and distribution across provinces

REMEDIATION AND REHABILITATION – RECOGNISED HIGHLIGHTS

Besides the above introduction on successes and overview on results there are a plenty of importantremediation projects at national level. However this is to provide two examples, which are as well internationally recognised,the most important landfill clean-up at "Fischerdeponie" and the rehabilitation project at the "gasworks Simmering", which was the starting point for revitalising an urban quarter at the city of Vienna well known nowadays for its architecture and in fact is an ongoing story of a "managed site".

With regard to the site "Fischerdeponie" a hydraulic barrier was installed as a first emergency response in 1989. Due to legal obstacles it took until 2001 for the remediation to start.In total 940.000 t of domestic waste, 15.000 barrels and 1,1 Mio. tcontaminated soil had been excavated and130 Mio. EUR were spent. Up to now 100% of the costs have been paid by public money and claims for compensation are before courts.

The largest manufactured gas plant in Austria was located in Simmering, the 11th district at the south-east of Vienna, covering an area of 325.000 m^2 and produced gas from 1899 until 1975. The major activities resulting in soil contaminationthe carbon gas cleaning, tar oil separators and storage tanks, ammoniac cleaning and, storage, and several other product storage tanks (e.g.naphthalene, benzene). During the early 90ies it was an urban planning decision to revitalise the area of the former gasworks. Since industrial and commercial reuse of the different sectors within the area is initiated sequentially. At the core and as a flagship of revitalisation the city of Vienna decided to reuse the 4 big gas storage tanks (see figure 3). As a result these historical brick stone structures are nowadays combined to modern architecture, which serves as a commercial centre and provides flats for residential use at upper floors. Since the late 90ies aseries of projects combiningsoil decontamination and groundwater remediation are ongoing. Since early 2014 a hydraulic barrier is under operation, which connected to a big water treatment plant remediates up to 55 l/s groundwater.

Fig. 3.“Gasworks Simmering” after rehabilitation - (source: Environment Agency Austria)

CHALLENGES FOR MANAGING HISTORICAL CONTAMINATION

Besides the successes with regard to the most hazardous sites and the generally reasonable progress of the Austrian remediation programsince 1990, it is obvious that in the near future changes not only by the legislative framework but even more important in strategies and practices will be necessary. In particular against the background of frequent shortages in public budgets andalso limitationsin private investments, it is expected that investigation and remediation will need to get more flexible and adaptive.Thus the national programme in Austria will need to improve its efficiencyfor realising savings in terms of money and time.

One of the major challenges already nowadaysis to establish strategies to organise investigation for larger numbers of smaller or less hazardous sites. This calls for tailored and more targeted investigation projects resulting in decisions and actions more quickly and at reduced expenses. To cope withsuch ambitionsintegrated investigation projects, which are eitherregionally focused or on a larger number of sites sharing a similar contamination pattern are intended and pilots have been launched already. However besides such strategic approaches for accelerating investigation, key for improving and implementing new practices needs to build on experiences and knowledge established during the last 25 years.

With regard to remediation a moderated discussion process resulted in publishing a “Vision on Contaminated Site Management” (2009), which describes key principles for introducing risk-based land management in Austria. Referring to that vision and given the necessary legislative changes will follow soon, it is expectedthat the number of historically contaminated sites needed to be managed under the national program can be limited to2.500.Theaccording total investment is estimated by 5 to 6 billion EURO. Finallythe long-term policy target definedis that by 2050 all seriously contaminated sites aremanaged suitably. In general this might involve any action of decontamination, containment, monitoring and combined measures. Hence improved practices and an efficient use of remediation technologies will be crucial. Furthermorethe general public and investors need to accept, that remediation projects will aim to reduce contamination and minimise risks, but not any morewill reach out for cleaning-up sites completely. Even if technically feasible a 100% elimination of contaminants usually costs an enormous amount of money and time. Reducinghistorical contamination by 80 %is generally less costly than efforts to get rid of the last 20%. So policy and citizens need to recognise that cost effective remediation is different fromtotal clean-up of the contaminants. Possible conflicts and questions arise with regard to environmental safety and legal security, both being also crucial aspects for site owners and investors. However in accordance to the BATNEEC-principle, which means the use of "best available technologies, not entailing excessive costs", contamination will need to be reduced to such an extent necessary for establishing a good environmental status and safe site conditions for reuse.Nevertheless these approaches will also call for better interfaces between contaminated site management, regional development andspatial planning.

NATIONAL REFERENCES (AVAILABLE ONLY IN GERMAN)

- WRG (1959): Water Act
- GeWO (1973): Industrial Code
- ALSAG (1989): Law on Contaminated Site Remediation
- AWG (1990): Waste Management Act
- BMLFUW (2009): "Vision on Contaminated Site Management" (2009)

FURTHER REFERENCE

- "Roadmap on Resource Efficiency" (EC(2011)21, 26.01.2011)

OLD ENVIRONMENTAL BURDENS IN THE CZECH REPUBLIC - DEVELOPMENT AND PERSPECTIVES

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At such a relatively small territory we have about 9 000 sites contaminated mainly in consequence of industrial activities developed here for several hundreds years. Activity of the industrial enterprises led to contamination of soils and ground water in thousands of sites in the Czech Republic. Also army bases, especially airports, were often heavily contaminated. Many of the contaminated sites is possible to consider as Brownfields. After the 1989, the political changes enabled the clean-up programmes to be started in our country. A great problem in elimination of environmental burdens from the past in the Czech Republic is the lack of an unambiguous legislative framework, that would permit a complex solution for all legal entities. The basic principle implemented in elimination of environmental burdens arising nowadays is that the burden should be eliminated by the party that caused it (the "polluter pays principle"). One of the key difficulties lies in burdens from the past for which the responsible party no longer exists or is not capable of eliminating the burden. In this case remediation process carried out using a variety of programs using a variety of financial resources.

The best results were achieved in remedy of contamination connected with the process of privatization and with the stay of the former Soviet Army. In the former case, decontamination measures are paid from the National Property Fund (now from the Ministry of Finance) and in the latter, from the state budget. In the period 1991 and 2014, Government of the CR approved 324 „remediation“ contract guarantees. Remediation works were finished at 153 sites and payments were made in an amount of 2,2 bil. EUR. Concerning Soviet Army, the sites with the most extensive contaminated areas and the highest risk levels include the former Hradčany airport in the former military training area of Ralsko and in the original training area of Mladá in the vicinity of Milovice. Clean up the stay of the former Soviet Army cost 60 mil EUR yet.

Another source of funding for the remediation process are EU Structural funds that can be used to remediation of sites owned by municipalities and sites contaminated by non-existent polluters (e.g. bankrupt companies, closed mines, brownfields etc.). Eligible costs are remediation activities and preparation activities - including Risk Assessment studies. In the Period 2007-2013 were invested 311 million EUR (from EU funds it was 259 million EUR), now in the period 2014-2020 it will be about half.

The strategy for elimination of environmental burdens from the past in the Czech Republic is based on the principles of the environmental policies of the MoE. The MoE issued Methodical Directives which laid down criteria for assessing the danger of pollution of the soil and groundwater and standardized the procedure for preparing the risk analysis.

One of the basic principles includes finding a socially acceptable level of environmental and health risks. This approach is based on the fact that the attaining of "zero risk" (e.g.absolute elimination of the contamination) is not always necessary from the standpoint of the environment and is usually associated with extremelly high costs. A second important principle is based on future use of the territory (i.e. so that it is "suitable for use"). In some cases, where decontamination is technically difficult to solve or financially unacceptable, consideration can even be given to an approach in which it is necessary to modify the subsequent use of the site. The Czech Environmental Inspection, as the independent administrative body of the MoE, on the basis of the results of risk analysis, issues a site-specific remedial order, in which the extent of the environmental burden is specified and the site clean-up standards and deadlines are delimited. The effectiveness of means expended for remediation of environmental burdens from the past is ensured by professional supervision organizations.

In past years database entitled the "Register of the Past Environmental Burdens" was created at the MoE. The database has been installed on the MoE server and is intended for employees of the MoE, local authorities and the general public, is updated regularly and includes information about the environmental damage and closed landfills.

In order to provide additional resources the MoE this year was declared a national environmental program, which is designed, among other things, to clean up illegal landfills and old ecological burdens owned by individuals.

The remediation system of environmental damage from the past is open and continuous process; further development and improving of which depend on preparation of laws, financial sources, technological progress in remedyiing technologies, field sampling, data analysis and data interpretation. The elimination of environmental burdens from the past leads to an improvement of the environment, where preference is given especially to the elimination of actual or potential sources of contamination of the groundwater. In addition, foreign investors prefer companies where the absence of environmental burdens can be unambiguously demonstrated.

SOIL POLICY AND DEVELOPMENTS IN THE MANAGEMENT OF CONTAMINATED SITES IN EUROPE

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KEYWORDS
Contaminated sites, indicators, industrial chemicals, priority, risk assessment, environment, human health

ABSTRACT

European laws (Water Framework Directive, Waste, Industrial Emissions and Landfill Directives, REACH and CLP Regulations of chemicals) do not address all the soil threats in a comprehensive way and not all Member States have specific legislation on soil protection. Article 191(2) of the Treaty on the Functioning of the European Union (TFEU), Union policy on the environment aims at a high level of protection taking into account the diversity of situations in the various regions of the Union, and is based on the precautionary principle and on the principles that preventive action should be taken, that environmental damage should, as a priority, be rectified at source and that the polluter should pay.

This paper illustrates the progress with the management of contaminated sites in Europe. It identifies local soil contamination as an important threat to human health and ecosystems. It aims to inform policy makers, professional practitioners, researchers, citizens and the media on the various Directives and projects related to soil protection. This paper is based on the JRC Reference Report "Progress in the management of contaminated sites in Europe" where data were collected from the National Reference Centres for Soil in 39 countries belonging to the European Environment Information and Observation Network (EIONET) during a campaign organised by the JRC European Soil Data Centre in 2011-2012. A set of indicators contributes to the Core Set Indicator “Progress in the Management of Contaminated Sites” (CSI 015) of the European Environment Agency (EEA), which is used for reporting on the State of the Environment.

The paper gives also an overview of the European Programmes related to soil and the funding possibilities by Horizon 2020, LIFE, EUREKA and the European Regional Development Fund.

EUROPEAN LEGISLATION AND SOIL PROTECTION

European environmental policy is one of the policy areas mostly developed since the last decade. It is well recognised that environmental problems go beyond national and regional borders and can only be resolved through collective actions at EU and international level. From an initial focus on chemical pollutants and impacts, environmental policy is moving into an integration phase, with the emphasis on understanding and addressing the pressures on the environment and examining the effects of different policies and behaviour patterns. Priorities have been set for water, air, waste, and chemicals where several Directives and Regulations have been implemented in Europe. However Water Framework Directive, Waste, Industrial Emissions and Landfill Directives, REACH and CLP Regulations of chemicals do not address all the soil threats in a comprehensive way and not all Member States have specific legislation on soil protection. Article 191(2) of the Treaty on the Functioning of the European Union (TFEU), Union policy on the environment aims at a high level of protection taking into account the diversity of situations in the various regions of the Union, and is based on the precautionary principle and on the principles that preventive action should be taken, that environmental damage should, as a priority, be rectified at source and that the polluter should pay.

The Soil Thematic Strategyexplains why further action is needed to ensure a high level of soil protection, it sets the overall objective of the Strategy and describes what kind of measures must be taken. Because not only do biodiversity loss and the degradation of ecosystems in the Union have important implications for the environment and human well-being, they also have impacts on future generations and are costly for society as a whole, particularly for economic actors in sectors that depend directly on ecosystem services. Its overall objective is the protection of soil functions and sustainable use of soil, based on two guiding principles:

- Prevention of soil degradation
- Restoration of degraded soils

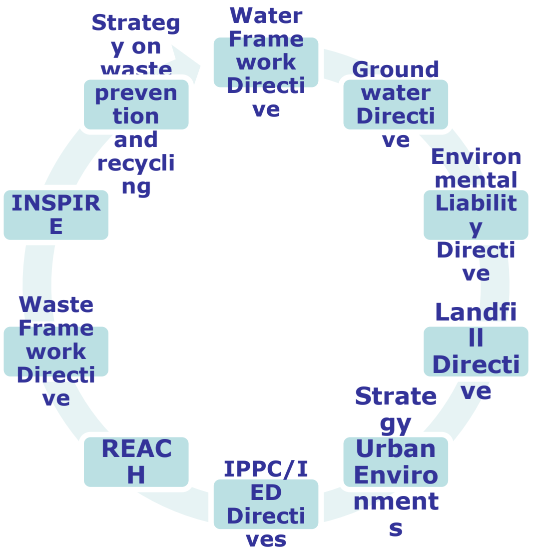

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Fig. 1. European Legislation related to the protection of the soil environment

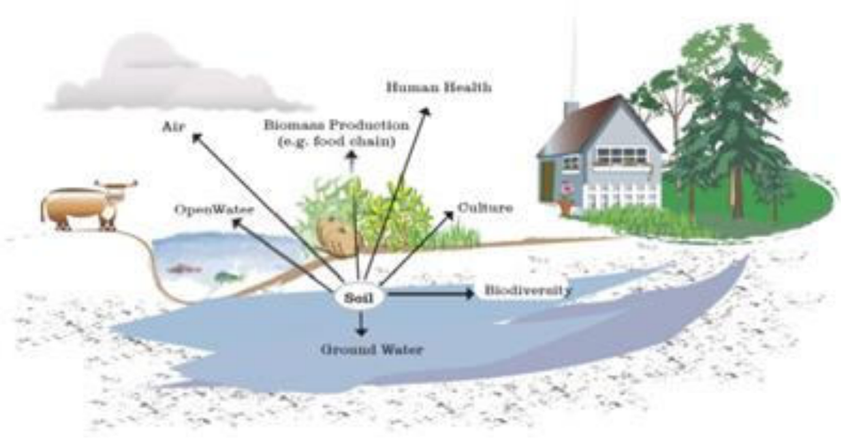


Fig. 2. Source courtesy "Soil protection, the story behind the Strategy". Office for Official Publications of the European Communities, 2006. ISBN 92-79-02066-8

The Soil Thematic Strategy (2006) sets out the four pillars of EU soil policy:

1. Framework legislation with protection and sustainable use of soil as its principal aim;
2. Integration of soil protection in the formulation and implementation of national and Community policies;
3. Closing the current recognised knowledge gap in certain areas of soil protection through research supported by Community and national research programmes;
4. Increasing public awareness of the need to protect soil.

After six years of the Soil Thematic Strategy the EU Commission has released a report (2012) on implementation of the Soil Thematic Strategy and on-going activities which presents the current soil degradation trends both in Europe and globally, as well as future actions needed to ensure its protection.

On May 2014 the European Commission has withdrawn the proposal for a Soil Framework Directive, REFIT Communication COM(2013) 685, 2.10.2013. Nevertheless, the Commission remains committed to the objective of the protection of soil and will examine options on how to best achieve this. Any further initiative in this respect will however have to be considered by the new college (2014-2015).

The European Commission has recently defined its policy vision in order to bring greater appreciation of the value of soil at all levels of society:

- Soils across Europe will be managed sustainably and pressures leading to degradation will be reduced to ensure the provision of essential services for current and future generations.

- Understanding that the competition for land should reflect the value of soil, especially in urban environments where vital soil functions should be maintained.
- Improved management of agricultural soils to ensure food security and safety while playing a greater role in the mitigation of the consequences of climate change.
- Reduce and prevent soil pollution (including dealing with historical contamination).
- Recognize the value of soil biota and the need to protect and enhance soil biodiversity.
- Need to focus attention on priority areas – but need to understand trends and impacts of degradation processes.
- Need robust and current evidence base to guide those who are actively managing land surfaces and support regulation and incentives where necessary to drive further action.
- Need for systematic and harmonized (regular) data collection.
- Need for societal push (policies to support awareness and education).
- Pan-European approach still valid due to indirect consequences of soil loss.

The Environment Commissioner Janez Potočnik at the conference on 'Land as a resource' in Brussels on 19 June 2014 has highlighted the importance of good land management to address European and global challenges, particularly in view of an increasing world population. The conference has tackled the shortcomings of the current European land use model, including conflicting policy drivers. A Communication on 'Land as a Resource' is expected to be released by the Commission on 2015. At present the impact assessment is ongoing and it will be first consulted with the new Commission and stakeholders. This Communication reinforce the need of raising awareness about the value of land as a resource for ecosystem services and proposes an analysis on how ecosystem services are affected by land take and land degradation, particularly in the context of global challenges (increase in population, food demand, bioenergy, climate change. Moreover the Communication is supporting further actions by evaluating current policy instruments.

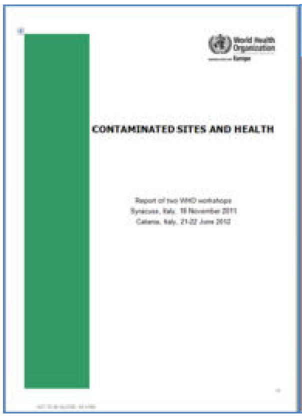
Fig. 3. Janez Potočnik at the conference on 'Land as a resource' in Brussels on 19 June 2014

MANAGEMENT OF CONTAMINATED SITES IN EU

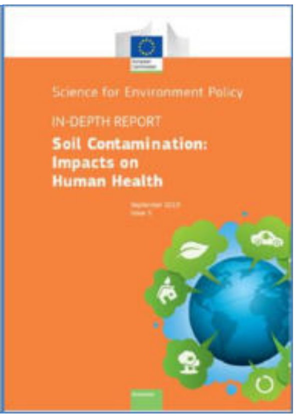
The Soil Thematic Strategy establishes a framework and common objectives to prevent soil degradation, to preserve soil functions and to remediate degraded soil. Under this strategy risk areas and polluted sites are identified and provision is made to remediate degraded soil. Proposes that EU Member States must also take steps to limit soil sealing, notably by rehabilitating brownfield sites and, where sealing is necessary, to mitigate its effects. In particular on contaminated sites, proposes that Member States must draw up a list of sites polluted by dangerous substances when concentration levels pose a significant risk to human health and the environment, and of sites where certain activities have been carried out (landfills, airports, ports, military sites, activities covered by the IPPC Directive, etc.). The Soil Thematic Strategy contains a list of these potentially polluting activities.

In the recent years public and private organisations are producing more evidences of the current and long-term impacts to human health and the environment due to the exposure to soil and groundwater contamination.
This is of particular importance at local scale, around contaminated sites but can have huge impact at regional and national scale.

Following the initiative of WHO meetings in Siracusa (2011) and Catania (2012); the European Commission DGENV has produced in 2013 a report on the <Soil Contamination, impacts on human health> and the Joint Research Centre has recently published the report on <Progress in the management of Contaminated Sites in Europe> (2014). This report has been produced by the Joint Research Centre (JRC) in collaboration with the European Environment Agency (EEA), 28 MS and 8 Associated Countries, the Common Forum on Contaminated Land and the Network of Industrially Contaminated Land in Europe (NICOLE). It presents the current state of knowledge about progress with the management of contaminated sites in Europe. It directly supports the EU Soil Thematic Strategy (COM(2006) 231), which identifies local soil contamination as an important issue. It presents facts, analyses and methods on the management of Contaminated Sites, which can inform policy makers, professional practitioners, researchers, citizens and the media.



CONTAMINATED SITES AND HEALTH



Science for Environment Policy

IN-DEPTH REPORT

Soil Contamination: Impacts on Human Health

JRC REFERENCE REPORTS

Progress in the management of Contaminated Sites in Europe

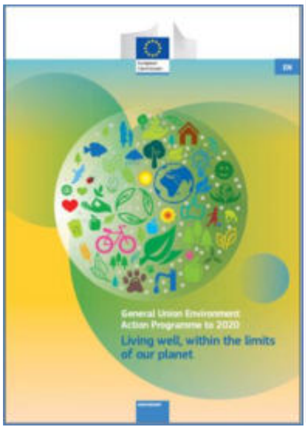
The report is based on data that were collected from the National Reference Centres for Soil in 39 countries belonging to the European Environment Information and Observation Network (EIONET) during a campaign organised by the JRC European Soil Data Centre in 2011-2012. The information presented in this report is based on a set of indicators which have been agreed on and used by the EIONET for more than a decade. This set of indicators contributes to the Core Set Indicator "Progress in the Management of Contaminated Sites" (CSI 015) of the European Environment Agency (EEA), which is used for reporting on the State of the Environment.

New parameters were introduced for the indicator “Progress in the Management of Contaminated Sites”. In previous data collection exercises, all parameters focused on the management steps (i.e. preliminary study, preliminary investigation, main site investigation, and implementation of risk reduction measures). In the 2011 data collection exercise, parameters on the number of sites were introduced, specifically the parameters “Potentially Contaminated Sites”, “Contaminated Sites” and “sites under remediation”.

EU FUNDING OF RESEARCH PROJECTS

While the Commission in May 2014 decided to withdraw the proposal for a Soil Framework Directive, the Seventh Environment Action Programme, which entered into force on 17 January 2014, recognises that soil degradation is a serious challenge. It provides that by 2020 land is managed sustainably in the Union, soil is adequately protected and the remediation of contaminated sites is well underway and commits the EU and its Member States to increasing efforts to reduce soil erosion and increase soil organic matter and to remediate contaminated sites.

Priority objective 1 of the 7th EAP is "to protect, conserve and enhance the Union's natural capital", and the recital 23. (…) refers to environmental considerations including water protection and biodiversity conservation should be integrated into planning decisions relating to land use so that they are made more sustainable, with a view to making progress towards the objective of 'no net land take', by 2050. Recital 25 says that "to reduce the most significant man-made pressures on land, soil and other ecosystems in Europe, action will be taken to ensure that decisions, relating to land use, at all relevant levels give proper consideration to environmental as well as social and economic impacts".



The Rio + 20 outcome recognises the economic and social significance of good land management, called for a 'land degradation neutral world'. *The Union and its Member States should reflect on how best to make such a commitment operational within their respective competencies. The Union and its Member States should also reflect as soon as possible on how soil quality issues could be addressed using a targeted and proportionate risk-based approach within a binding legal framework. Targets should also be set for sustainable land use and soil. In more, recital 28 says that "In order to protect, conserve and enhance the Union's natural capital, the 7th EAP shall ensure that by 2020 (...) (e) land is managed sustainably in the Union, soil is adequately protected and the remediation of contaminated sites is well underway." And continuous, "this requires, in particular (...) (vi) increasing efforts to reduce soil erosion and increase soil organic matter, to remediate contaminated sites and to enhance the integration of land use aspects into coordinated decision-making involving all relevant levels of government, supported by the adoption of targets on soil and on land as a resource, and land planning objectives*".

Interested parties can apply to four main EU Funding of Research Programmes: LIFE, H2020, EUREKA and European Regional Development Fund.

The LIFE Regulation EU/1293/2013 establishes the Programme (2014-2020) for the Environment and Climate Action (LIFE) and the following Implementing Decision, in its Annex III (c) Thematic priorities for Resource Efficiency, including soil and forests, and green and circular economy.

The new LIFE Regulation (2014-2020) EU/1293/2013 of the European Parliament and of the Council of 11 December 2013 establishes the Programme for the Environment and Climate Action (LIFE).
This programme promotes the implementation and integration of environment and climate objectives within European policies and Member States practices.

It comprises two sub-programmes: Environment and Climate Action.

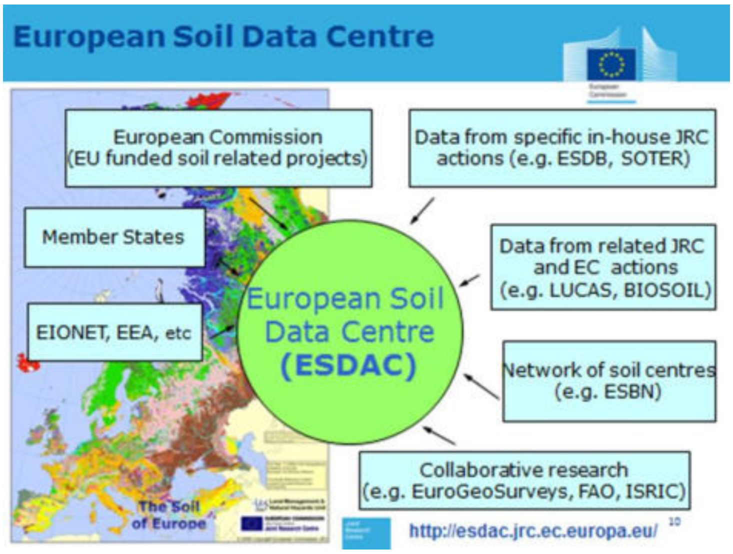
The Sub-programme Environment includes as priority areas: a) environment and resource efficiency, b) nature and biodiversity, and c) governance and information. Budget: 2.592,5 M€

The Sub-programme Climate Action includes as priority areas: a) mitigation to contribute to the reduction of greenhouse gas emissions; b) adaptation to support the efforts leading to increased resilience to climate change; c) Climate governance and information. Budget: 864,2 M€

Every priority area is translated into thematic priorities for example the thematic priority for "Resource Efficiency" includes project topics on soil, forest, and green and circular economy, for funding in the multiannual work programme 2014-2020.

The Union contribution to the multiannual work programme is of approximately 500 M€ for the priority area ‘Environment and Resource Efficiency’. As referred to "Soil" calls for projects are designed to achieve better soil management (avoiding compaction and contamination, etc.) at the local, regional or national level. The methods used can include monitoring tools and practices or the improvement of administrative and legal frameworks and to projects that develop and implement cost-effective support tools and schemes for the identification of contaminated sites at regional or national level.

LITERATURE



1. The European Soil Portal is an integral part of the European Soil Data Centre, which is one of the **tenenvironmental data centres in Europe and is the focal point for soil data at European level.** This European Soil Portal contributes to a thematic data infrastructure for soils in Europe. It presents data and information regarding soils at European level. It connects to activities within JRC concerning soil (JRC SOIL Action). It serves also as a vehicle to promote the activities of the European Soil Bureau Network. Spatial data collection and processing within this infrastructure is performed according to emerging ideas behind the INSPIRE (Infrastructure for Spatial Information in Europe) initiative.
2. Soil Datasets:The European Soil Portal contains currently many soil data, maps, information, Atlases and applications; most of the offered data are at European scale, while, when possible, links to national or global datasets are provided.
3. Soil at JRC: Soil activities within the JRC are concentrated in a specific JRC Action, called FP7 "Soil Data and Information Systems" or SOIL. Thematic Assessment Soil in the "State of Environment Report (SOER2010) is also available.
4. Documents - Publications: European Soil Bureau Research Reports, JRC Scientific and Technical Reports, Papers in Journals, Publications in Conferences, Posters and Publications in CD-ROMs, Glossary of Soil Terms.
5. Soil Projects: many past and current projects relate to the soil activities of JRC.
6. Soil Themes: covers various results for different soil themes such as Erosion, soil Organic Carbon Content, Salinisation, Landslides, Soil Compaction, Biodiversity and soil Contamination.
7. European Soil Bureau Network (ESBN): is a network of soil institutes supporting the JRC soil activities.
8. International Cooperation: presents the most Important International Cooperations that Soil Action is participating (Global Soil Partnership, Global Soil Biodiversity Initiative, GlobalSoilMap.net, Sino-EU Panel on Land and Soil).
9. Events - Presentations in various events(Conferences, Workshops, Meetings, Summer Schools) which are related to the work that the Land Management Unit is doing in relation to the European Soil Bureau Network. Calendar of future events is also available.

10. Awareness Raising Our Goal as Soil Action is to Establish an action plan for the development of measures/programmes/initiatives to raise awareness of the importance of soil across European society (i.e. policy makers, general public, universities, schools, industry, etc.).
11. What's new? Chronology of items added to this soil portal. Get the NEWS in XML XML format and the monthly Newsletters.
12. Utilities - Various : A mailing list has been set up in order to keep interested persons up to date with the latest contents on this site. Other Tools such as the Search Engine are also available.
13. Team - Action SOIL: the people at JRC behind the soil activities.
14. Links: key pointers to soil related bodies and International Organisations.

INFORMATION SYSTEM OF CONTAMINATED SITES IN SLOVAKIA

Erich Pacola[1] – Milan Schmidt – Ivan Dulgerov

[1]Slovak Environment Agency, DATACENTRE – Centre of Environmental Data and Information Services, Banská Bystrica

KEYWORDS
Contaminated sites, information system of public administration, integration of information systems, web services, network services

ABSTRACT

Information System of Contaminated Sites (ISCS) represents a basic and an official platform for records of contaminated sites in Slovakia. A register of contaminated sites, supports the content of the information system. It records the life cycle of CS and all information resulting as a consequence of processes defined by Act no. 409/2011. A register of contaminated sites consists of section A - comprising records of potentially contaminated sites, section B – comprising records of contaminated sites and section C – comprising records of remediated and reclaimed localities. Currently (on 16 April 2015) register contains information on 1,762 localities of which 902 are classified into the section A, 279 in the section B and 759 into the section C. The project of ISCS integration with registers or databases of the Slovak Ministry of the Environment and other government departments was launched in 2010. As a result of feasibility study 13 registers were chosen and integrated with ISCS. In terms of integration principles, it was introduced system integration on the basis of sharing web or network services. This minimises mutual dependence on existing applications and offers the reuse of already constructed services.

WHY INFORM ABOUT CONTAMINATED SITES?

It is estimated that there are approximately 2.5 million contaminated sites in Europe. For these sites, contamination may arise from existing ground soils, or indeed from pollution originating in bedrock. For such sites, the danger of pollutants spreading into surrounding areas may be anticipated. It is, therefore, imperative that these sites are thoroughly investigated, a risk assessment being carried out to inform the public concerning the whereabouts of these locations, as well as importantly, providing information regarding current and planned efforts to mitigate harmful effects upon the health of the public and the quality of environment.

Those citizens who wish to purchase land for house building, or plan to buy existing property, should have open access to information regarding whether the ground or property is close to sites where the underground water supply, bedrock or soil quality are not endangered and onto which there is the potential for pollution to spread. Development plans held by local authorities should take into account any hazards, without doubt, of course, the presence of any contaminated site (onwards referred to as CS).

State and public administration bodies, in the sector of process control for environmental protection or the approval of development plans, must have access to information obtained from specialised geological assessment undertaken on contaminated sites. This concerns, primarily, the results of geological surveying of sectors of the environment on CS, expert analysis of CS risks on human health and the environment, information relating to the progress and method of remediation of CS and results from the monitoring of geological factors. In other words, monitoring the extent of pollution, both during and after remediation. Only in this case, may representatives of state and public administration bodies be successful in the planning of future precautions to lower risks due to the presence of CS, when redistributing investments for the removal of pollution caused by CS or when controlling remediation work and the reclamation of previously contaminated sites.

WHERE TO FIND INFORMATION ON CONTAMINATED SITES

Information System of Contaminated Sites (onwards 'ISCS') represents a basic and official platform for records of contaminated sites in Slovakia. Contaminated site (onward referred to as CS) is defined as a site, where hazardous substances caused by human activities, poses a significant risk to human health or to the environment, soil and groundwater, except environmental damage. ISCS is a part of the public administration information system according to paragraph 20a, section 1 of the Act no. 569/2007 on geological work (geological law) as amended (onwards referred to as ‘Act no. 569/2007’).

The basic components of ISCS are stated in regulation of the Slovak Ministry of the Environment, no. 51/2008 as amended, which implements the geological law.

They are:
a) A state program of contaminated site remediation.
b) A register of documents related to contaminated sites.
c) A register of contaminated sites, consisting of:
    1. Section A - comprising records of potentially contaminated sites,
    2. Section B – comprising records of contaminated sites,
    3. Section C – comprising records of remediated and reclaimed localities.

Since 2010, a significant amount of work has been carried out on various of the new ISCS services. They are currently operational and make up an integral part of the information system. The basic applications and content of the ISCS, comprise the following services:

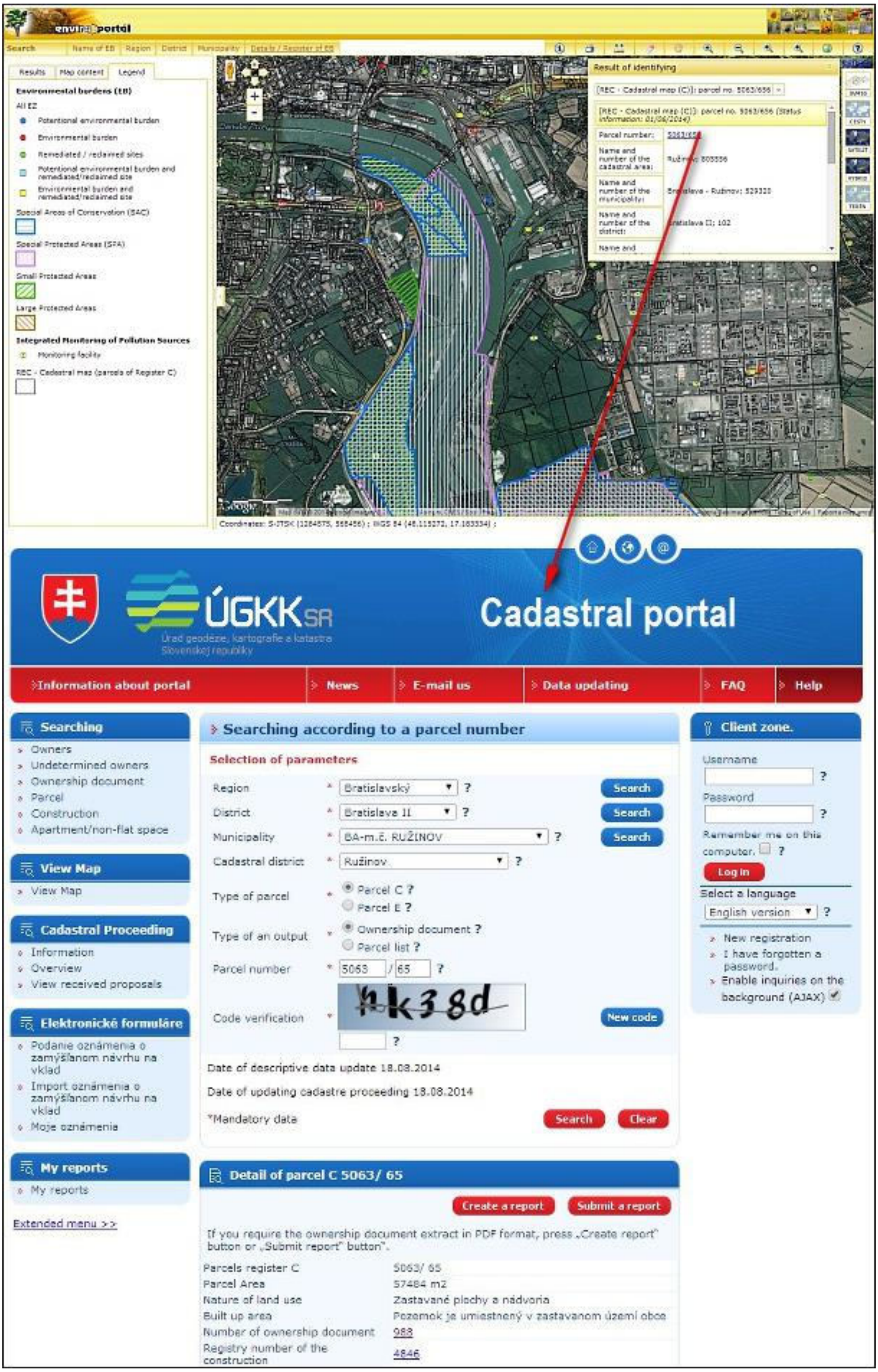
1. An Enviroportal, which serves as the common internet access point designed to provide environmental information and E-services. In terms of a development conception of IS at the Ministry of Environment of The Slovak Republic, for the years 2014 to 2019, it is defined as a second level portal of the Central Government Portal. Website: http://enviroportal.sk/environmentalne-temy/vybrane-environmentalne-problemy/environmentalne-zataze/informacny-system-ez
2. A Register of contaminated sites, supporting the content of ISCS. It records the life cycle of CS and all information resulting as a consequence of processes defined by Act no. 409/2011. The register enables the search and subsequent presentation of descriptive information on CS in the form of lists, reports and registration sheets (http://envirozataze.enviroportal.sk/) or information can be displayed in the form of maps and spatial data positioning on these maps (http://envirozataze.enviroportal.sk/Mapa/).
3. An atlas of remediation methods, completed in 2011 by the State Geological Institute of Dionýz Štúr. Contains a series of remediation methods for the elimination of contaminated sites and is accessible to the general public in the form of a web application. The application enables the user to search for information according to the type of remediation method and contaminating substance. It interactively connects to remediated localities contained in the Register of contaminated sites, including appropriate methods of remediation applied at the given localities. Website: http://envirozataze.enviroportal.sk/Atlas-sanacnych-metod
4. Under the direction of the Ministry of the Environment, Act no. 569/2007 concerns both a register of professional competence (i.e. register of acknowledged specialists competent to undertake geological work) and a register of geological licenses (i.e. register of geologically authorised individuals, entrepreneurs and legal persons). It concerns indexes of the aforementioned who have the right to perform geological work in the territory of the Slovak Republic and a list of competent specialists complete with their contact details.
   Website:
   http://envirozataze.enviroportal.sk/RegisterPovoleni/GeolFyzOs.aspx
   http://envirozataze.enviroportal.sk/RegisterPovoleni/GeolPravOs.aspx
   http://envirozataze.enviroportal.sk/RegisterPovoleni/RegisterOdbSposob.aspx
5. An Integrated application interface which accesses, via the ISCS, information held in other data sources consisting of relevant databases and registers of the public administration information system. (onwards referred to as PAIS). This concerns an interface which enables exchange of records between registers of data sources and the ISCS. Mutual communication of the application interface for administration of these records runs in actual time and is independent of the active participation of users.

REGISTER AND DATABASE CONNECTION WITH ISCS

Based on the results of the feasibility study, a process was launched whose output was the contractual arrangement of technical work for the connection of ISCS with data sources which are administered by the Ministry of Environment and Ministry of Agriculture and Rural Development of the Slovak Republic. The connected systems were arranged into the following groups:

- Records of monitoring systems:
  - Integrated monitoring of pollution sources,
  - Partial monitoring system of geological factors - Subsystem 03, Anthropogenic sediment character of old contaminated sites

  - Partial monitoring system - Soil
  - Technical and safety supervision of Slovak water constructions.
- Records of protected areas of the Slovak Republic:
  - State list of specially protected parts of the countryside - protected areas and protected trees section,
  - EU member's network of nature protection areas - NATURA 2000,
  - A register of Ramsar Wetlands, UNESCO heritage sites and Biosphere reservations.
- Records for the support of environmental legislation:
  - Geofond digital archive,
  - Information system for the mining waste management
  - Information system for the prevention of major industrial accidents,
  - Register of landfill sites
- Basic spatial register and large scale maps:
  - Digital orthophoto maps of the Slovak Republic and detailed panoramic images of streets and roads of the Slovak Republic (Google Slovakia Ltd.)
  - Digital vector cadastral maps (Geodetic and Cartographic Institute, Bratislava)



Result of identifying

[REC - Cadastral map (C)]: parcel no. 5063/656

[REC - Cadastral map (C)]: parcel no. 5063/656 (Status information: 01/06/2014)

Parcel number:	5063/656
Name and number of the cadastral area:	Ružinov: 805556
Name and number of the municipality:	Bratislava - Ružinov: 529320
Name and number of the district:	Bratislava II: 102
Name and	

Coordinates: S-JTSK (1284575, 558456) ; WGS 84 (48.115272, 17.183334) ;

Searching according to a parcel number

Selection of parameters

Region *	Bratislavský
District *	Bratislava II
Municipality *	BA-m.č. RUŽINOV
Cadastral district *	Ružinov
Type of parcel *	● Parcel C ○ Parcel E
Type of an output *	● Ownership document ○ Parcel list
Parcel number *	5063 / 65
Code verification *	hk38d

Date of descriptive data update 18.08.2014

Date of updating cadastre proceeding 18.08.2014

*Mandatory data

Detail of parcel C 5063/ 65

If you require the ownership document extract in PDF format, press „Create report" button or „Submit report" button".

Parcels register C	5063/ 65
Parcel Area	57484 m2
Nature of land use	Zastavané plochy a nádvoria
Built up area	Pozemok je umiestnený v zastavanom území obce
Number of ownership document	988
Registry number of the construction	4846

Fig. 1. Identification of land plots affected by contaminated site B2 (013)/Bratislava-Ružinov - Slovnaft - surrounding area of the company. Connection to the Cadastral portal and verification of ownership rights.

EXPERIENCE GAINED FROM UNDERTAKEN WORK

The integration of systems, up to the present, belongs among the most difficult projects undertaken within the Slovak Environment Agency. Due to the diversity of systems included in the project, it was necessary to bring together experts, despite the wide variety of addressed domains and utilised technologies. The most difficult part, however, was not the technical realisation of work. Above all, integration required complex organisational arrangement of work. Domain experts had to be involved in the project from each organisation, as well as administrators of existing systems and developers (own employees), but especially from external sources. It was shown that processes which solved integration were not limited only to one section or department connected to the organisation (e.g. department of IT). On the contrary, process solving occurred across the whole organisational structure, that is, through every organisation, which in the end meant the solving of unforeseen events. In spite of this, realisation of the project contributed to the improvement of information exchange between public administration bodies, as well as towards the general public. Development of an application interface will enable easier and more effective implementation of new requirements in the future. (e.g. eGovernment activities).

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OVERVIEW OF THE GENERAL AND SPECIFIC ELEMENTS IN THE METHODOLOGY OF THE CONTAMINATED SITES INVENTORY

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

ABSTRACT

The methodology for the nationwide inventory of contaminated sites elaborated in the 1st stage of the National Contaminated Sites Inventory (NIKM) project represents a complex structure of principles, process steps, working procedures and manuals intented for completing the appropriate template records of a particular database system, process management and project control and for supervisory mechanisms.

With regard to the development in the field of informatics and information technology, the proposed NIKM solutions of the application support and database system (elaborated 4-5 years ago) seem to be technically and technologically outdated.

For further development it would be advantageous to divide the methodological documentation into two levels – more general – e.g. for tender purposes and official methodological guidance, and more specific - linked to the particular database system and to the specific inventory tools.

NATIONAL CONTAMINATED SITES INVENTORY (NIKM) PROJECT STATUS

The first stage of the NIKM project was finished by the end of June 2013. Its basic goals were completed incl. an elaboration of methodology and tools for territorial inventory; developed methodology and tools piloted and tested; collected and unified existing data sources containing information on contaminated sites from state territory; and a prepareddraft of the executive stage of the project.

The methodology of the nationwide inventory of contaminated sites was elaborated within the first stage of the National Contaminated Sites Inventory (NIKM) project [1] [2] [3] performed in the period 2009 - 2013 as a project of the Operational Programme of the Environment 2007-2013, Priority Axis 4 - The Improvement of Waste Management and the Rehabilitation of Old Environmental Burdens, the area of intervention 4.2. - The Rehabilitation of Old Environmental Burdens. The NIKM project was run by a project team composed by CENIA and several contractors resulting from in an open public tender process.

Individual outcomes and final project outcomes were finished in the summer of 2013 (for published results see e.g. [2] [3] [4] [5] [6] [7]). Detailed information from the project is publicly disclosed on the project web site: http://www1.cenia.cz/www/projekt/nikm.

APPLICATION SOLUTIONS - INVENTORY TOOLS

Proposed application support for inventory work phases [8] [9] consisted of:

- On-line application NIKM Editor – client environment available through a web browser. It allows record management in the central data warehouse, data editing, inserting of measurements and other findings.
- Off-line application NIKM Client – allowing field data collection.
- Web portalNIKM – for publishing data on contaminated sites for the general public and public administration.
- Central Data Warehouse.

2nd STAGE NIKM 2015-2020 SCHEDULE

In 2012-2014 we were not successful in obtaining co-financing for the 2nd stage of the NIKM project from the MoE (CENIA's founder), so that an application for the financial support to the Operational Programme of the Environment (OPE) could not be submitted. Time demands of the project in connection with the field work and hence the seasonal nature of most of the work were the main limiting factors for the realization, still at the end of the OPE 2009-2013. Given the need to cover the entire area of the Czech Republic with the inventory, the minimum requirement was the period of at least two years of inventory work. Because of the need to complete the work of the OPE 2009-2013 by mid-2015, it was finally decided to pospone the second stage of NIKM until the new programming period of the OPE [10]. In the program document prepared for the OPE 2015-2020, our National Inventory issue is a part of the Priority Axis 3 (Waste and material flows, environmental burden and risks), specific objective 3.4 (Complete inventory and eliminate environmental burdens).

By the end of 2020, in the part related to inventory, the greatest number of sites should be documented, and based on the information obtained, their prioritization should be done. Obtained data should be recorded into the information system used for state administration in the context of administrative proceedings, but also for professionals and the public.

The target value for the year 2023 is 8,952 contaminated sites being registered, incl. their priority ranking. A preliminary schedule of requests of the new OPE 2015 counts for submitting applications for the specific objective 3.4 in the first half of 2015.

PROJECT METHODOLOGY

Methodology for the inventory connected to the intended database NIKM and application tools is described in the 2nd stage of the NIKM project (especially in the chapters: Inventory methodology, Organization and Management of the inventory) and is in the form of a set of NIKM methodological materials that define the obligatory process of the inventory [8]. These are primarily documents "Inventory Methodology" (about 60 pages), "Organization and management of the inventory" (about 120 pages) and "Manual for the inventory" (about 70 pages) – see Fig. 1. The methodology was designed to fulfil the demand of completeness for all of the inventory process, and to enable a comprehensive idea for the continuity and sequence of phases and activities carried out within them and the links among them.

Reflecting the quick development in the field of informatics and information technology (both SW and HW) we have to admit that the proposed NIKM solutions for the application support and database system (elaborated 4-5 years ago) seem to be technically and technologically outdated.

Besides the NIKM database and NIKM application tools upgrades there is also another solution - a modernization of the existing Contaminated Sites Database System (SEKM). For being appropriate for the contaminated sites inventory, this “new SEKM” has to contain an “inventory module”.

In further development of any of the two options (NIKM or SEKM) it is advisable and advantageous to have methodological documentation for the contaminated sites inventory divided into two levels:

- the first - more general – for the purpose of tender specification documents and for the use in the MoE methodology guidance documents;
- the second – more specific – related to the individual database system usable for the contaminated sites inventory and for the specific inventory tools.

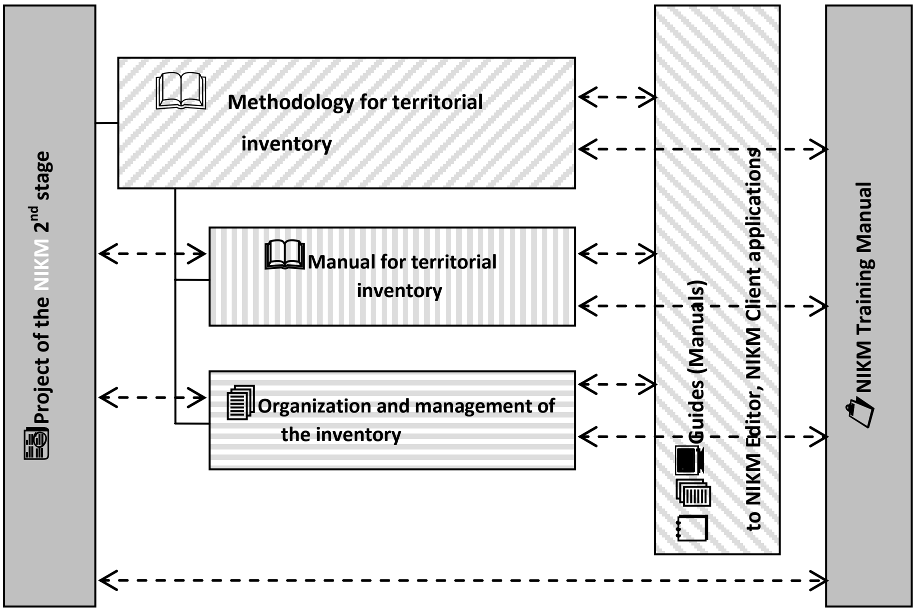

Fig. 1. Relationships among the documents composing a set of NIKM basic methodological documents designed in the project draft form 2012 [9].

In a more general way NIKM methodology (e.g. for the purpose of tender documents for public procurement) should include references to principles such as:

- **Optimal multiplicity of information sources** (using all available sources of information on contaminated sites and on indications of contamination).
- **Improve information quality** to a level enabling decision (for example whether a contamination indication is evaluated as a suspicious site or whether after further examination it reaches the status of contaminated site with a corresponding priority ranking).
- **Multistage control and verification** (as in the processing of inventory records, as in the transferring of the resulting records into the central database of contaminated sites).
- **Phase by phase methodological approach** within the inventory implementation. The mapping process is divided into several phases that build on each other in time and the subsequent implementation phase is conditioned by the completion of the previous phase: (1) The initial stage, (2) Information campaign, (3) Primary data analysis, (4) Data collection, (5) Priority evaluation and (6) Outcome documents elaboration (see Fig. 2).
- **Ongoing consultation** with the public and local governments.
- **Openness in obtaining evidence and information** about the inventory to the public.

The objective of the 2nd stage - the identification, registration and basic assessment of the largest possible ammount of contaminated sites and updating of the information on all known locations - is valid for any methodology and tools mix. The executive phases “Information campaign“, “Primary data analysis“, “Data collection“ and “Priority evaluation“ (see Fig. 2) are applicable for any methodological arrangement.

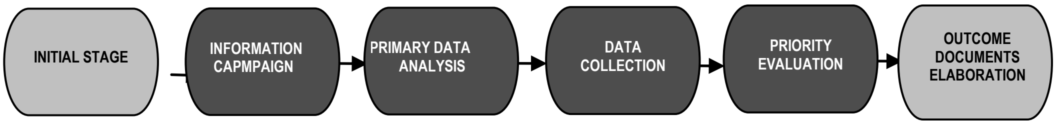

Fig. 2. Methodological phases and outcomes from the Territorial Inventory of Contaminated Sites [9]

In the case that we do not relate to a particular database system with its specific tools for inventory, we must modify methodological documents so that they can serve e.g. for the purpose of public procurement tender documents. Only general guidelines and procedures as well as links to publicly available specific manuals and documentation attached to a particular database application tool (like current SEKM Guidance [11]) should be left from the original methodology (as drafted in the project proposal [7] [8]).

Considered modification of the methodological documents scheme is shown in Figure 3.

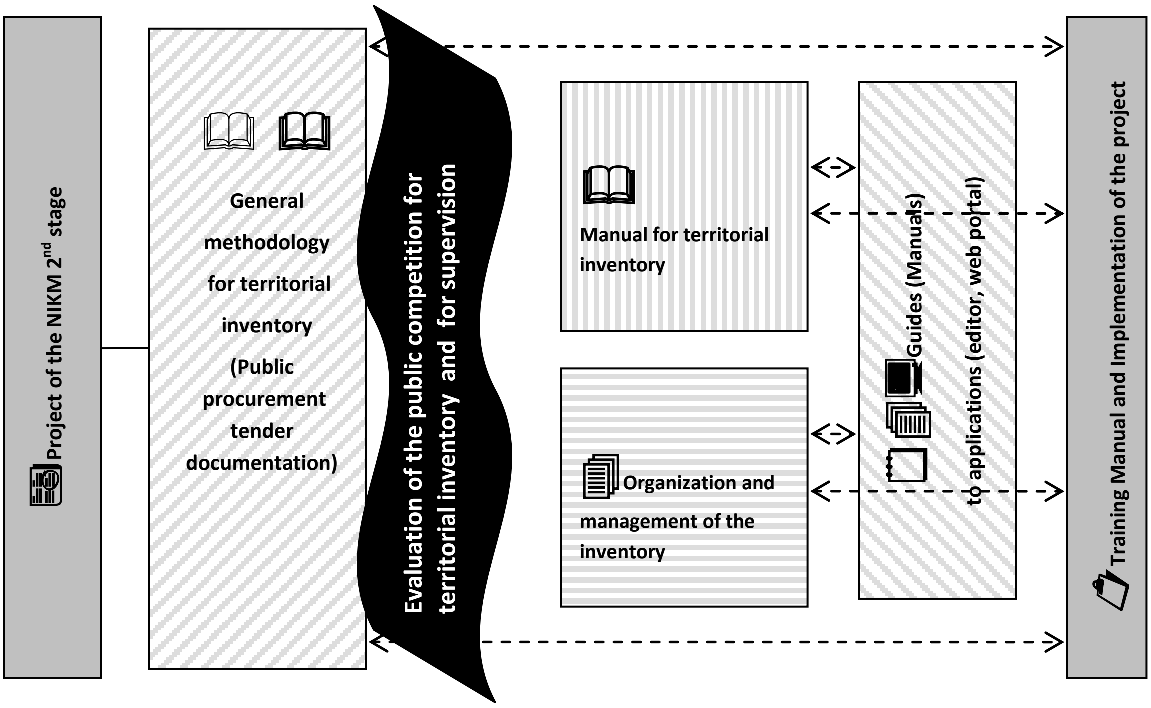

Fig. 3. Considered modification of the methodological documents scheme for the 2nd stage of NIKM

CONCLUSIONS

In the 1st stage of the project (finished in summer 2013) the project team created and verified methodology for the nationwide inventory. With regard to the development in informatics and information technology the proposed NIKM solutions of the application support and database system seem to be out-of-date. Besides the NIKM database and application tools upgrade, there is also a modernization of the existing Contaminated Sites Database System (SEKM) to be considered. This "new SEKM" would contain an "inventory module".
In further development it is advisable to have methodological documentation for the contaminated sites inventory divided into two levels:

- the first – more general – for the purpose of tender specification documents and for the use in the MoE methodology guidance documents;
- the second – more specific – related to the individual database system usable for the contaminated sites inventory.

The objective of the 2nd stage - the identification, registration and basic assessment of the largest possible ammount of contaminated sites and updating the information on all known locations - is valid for any methodology and tools mix.

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ESTABLISH THE GEO-DATABASE ON ECOLOGICAL HEALTH OF THE MILITARY SITES

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KEYWORDS
Contaminant, contaminated sites, geodatabase, database, environmental damage assessment, compensation.

ABSTRACT

In Mongolia, there are many contaminated sites caused by mining, industry, waste disposal, agricultural use and military activities, which is dangerous to human health and environment. The objective of this paper is to present a contaminated sites geodatabase of Mongolia. The purpose of the geodatabase is to integrate diverse data set produced by different organizations in multiple format, and to deliver the data to users in more efficient way. The geodatabase was developed using PostgreSQL and UML/Enterprise within the framework NATO/Project on "Establish the geo-database on ecological health of military sites.

The geodatabase of Mongolia contains soil and water contamination information caused mostly by mining and military activities. There are registered 283 sites. Each site record includes information on location, name and description of site, photos taken at site, sampling points, contaminant value, contamination assessment report and remediation works done. The geodatabase consists of 23 tables and 195 fields. This database provides online access and functions to search, update, retrieve data in table and map forms, download and report an issue to users with permission. A map module has the most commonly used GIS tools such as zooming, identifying, measuring, overlaying and printing.

The database has greatly assisted to monitor environment, identify the contaminated areas, assess damages, impact and potential risks, define compensation amount to be paid by polluter, and plan remediation measures.

INTRODUCTION

In Mongolia, pollution of air, water and soil is mostly caused by industries and factories, agriculture use and waste disposal. In 2010, methodology for assessing environmental damage and calculating compensation amount was approved by Minister of Environment. In 2012, “polluter pays principle” was enacted, which states that whoever produces pollution should bear the management costs to prevent damage to human and ecological health and all other associated costs. To implement the principle, Mongolia has made inventory of degraded and contaminated areas through surveying 1551 sites. Field study was performed by Ministry of Environment and Green development and Mineral Resources Authority during 2011-2014. Total of 283 sites were investigated as potential contaminated sites. In total, 1551 samples of water and soil were taken. Pollution information has been usually related to many organizations. Since 2013, the contamination site database has been developed within NATO funded project “*Establish the Geodatabase on ecological health of the military sites”.* The project was implemented jointly by Environmental Agency of Slovakia, Environmental Information Center, Institute of Geo-Ecology and Ministry of Defense of Mongolia. The purpose of this geodatabase is to integrate diverse contamination data set produced by different organizations in multiple format, to provide data to decision makers and public in more efficient way. The contaminated sites database helps to identify sites and polluter, monitor contaminant level, assess risks to human and environment, set priority, and plan rehabilitation work and site management.

METHODOLOGY

We developed the geodatabase in accordance with the existing environment policy and legal acts, standards to support decision making process, improve data sharing, ensure data interoperability and quality, complete and update data, and provide users with easy and efficient access to data and information service based on geodatabase. The database model was developed in UML/Enterprise Architecture diagram. The contents of database was defined in accordance with the environment protection law, government regulation on datasets, regulation and methodology to assess environmental damage and calculate compensation value. The database has contains data dictionary, which contains a list of all tables and field names in the database, data description and types, constraints, rules and relations to other data.

The database was developed using PostgreSQL. The map interface was developed with pMapper and Mapserver. The programs were written in PHP and Javascript. For the database development, we used open source software as PostgreSQL/PostGIS, Mapserver, Geonetwork, pMapper, GeoMoose and GeoMoose, based on their cost effectiveness, scalability, and capacities to extend. Programs and codes were developed using PHP, JavaScript. The geodatabase is Web/GIS based, ensuring data transparency, database accessibility and wide usage. All maps or layers which may be needed for contamination issue were entered to database and converted to UTM projection, which has been approved by the government to be the standard projection in Mongolia. The project geodatabase installed on the Environmental database server and accessible at www.eic.mn/envmonitor. The database is available in Mongolian and English.

Seven parameters (pH, As, Cd, Cu, Pb, Zn) were used for soil quality assessment, and 14 parameters (pH, EC, ORP, DO, NTU, Alk, F, Mn, Ni, Cu, Cd, Pb, As, Cr, Zn, Fe) for water.

THE DATABASE CONTENT AND STRUCTURE

The geodatabase 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 site, contaminants and risk assessment. The general data structure is shown in Figure 1.

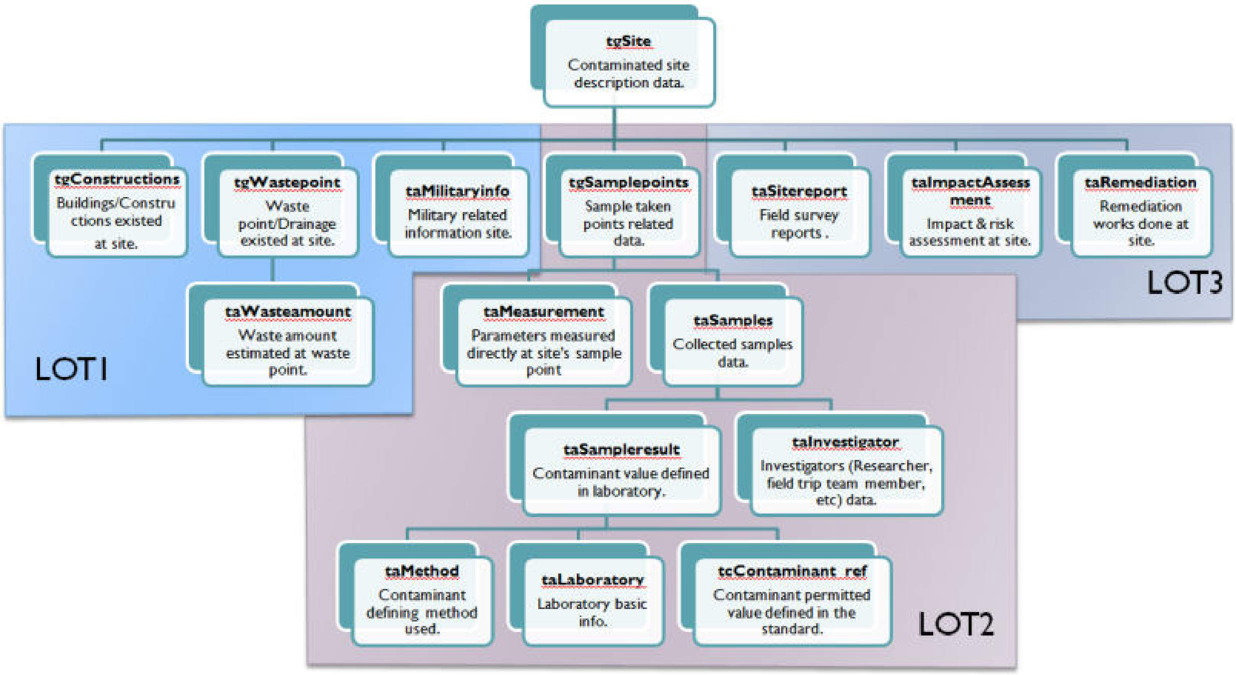


Fig. 1. Data structure

THE DATABASE INTERFACE

The database has the following subsystems as Data query, Data entry, Map/GIS and Report output. Fig. 2 shows the main page of the geodatabase interface.

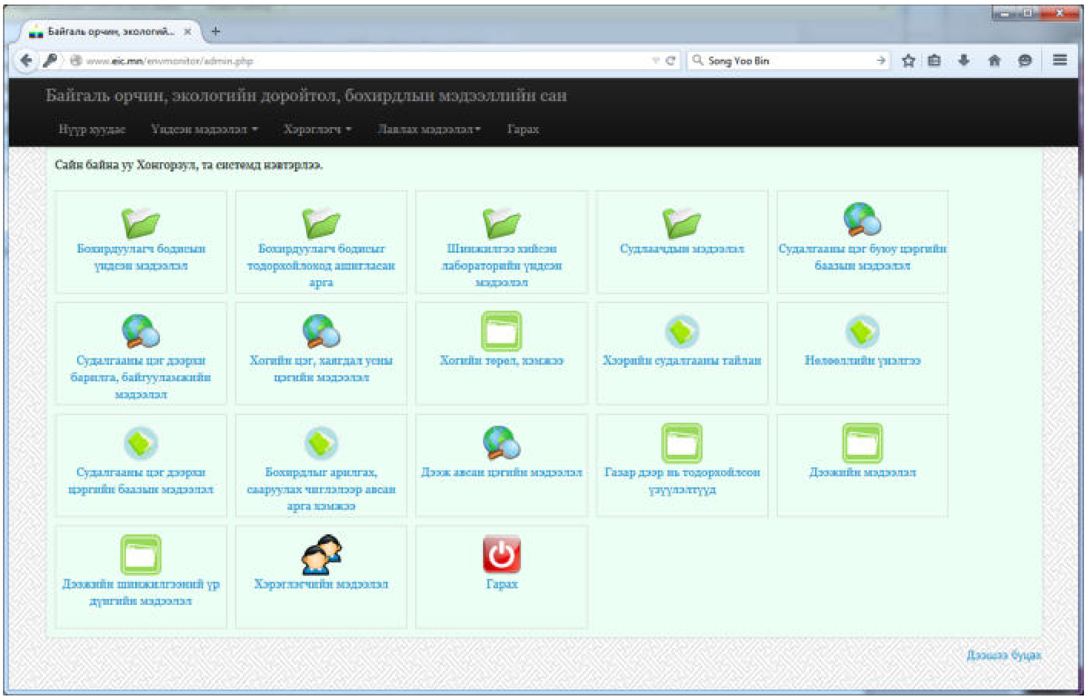
Fig. 2. Main web page of Contaminated sites geodatabase

*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 (Fig 3). Data will be sorted by clicking on the field name on top of the table. Browse button displays data in new window in more detailed way.

№	Contaminant name in Mongolian	Contaminant name in English	Contaminant's chemical formula	Subject related to contaminant permitted value	
1	1	2	3	4	Browse

Fig. 3. Data query interface page

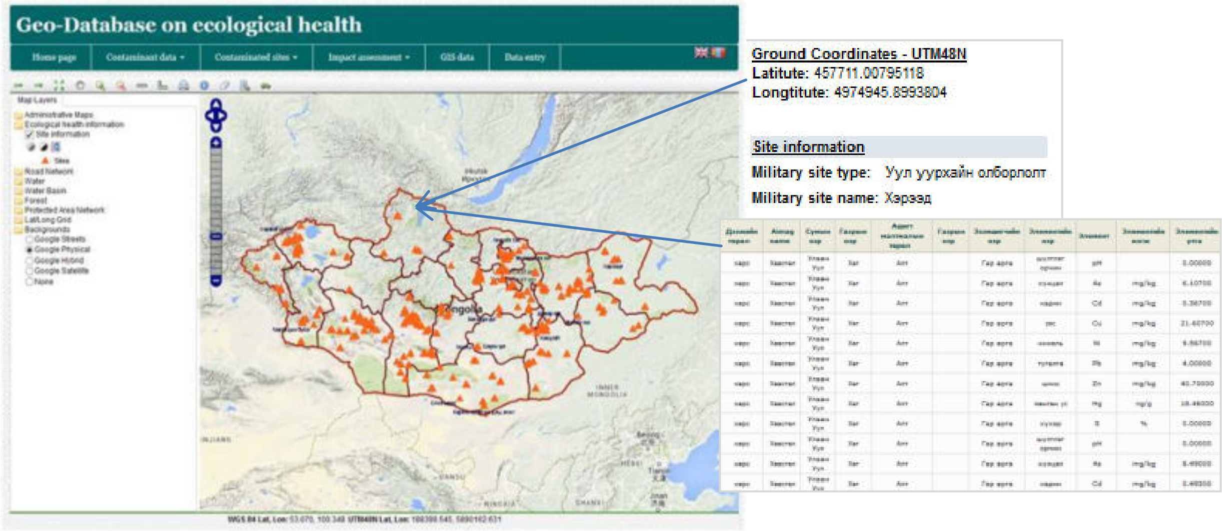
Data entering system. Data entry is allowed only for registered users. Therefore user registration module checks and allows users to access to system. Each user has limited access, depending their roles in the system. Each action performed by a user is recorded in a transaction protocol file. Data entry form is dedicated for each table. The data entry main interface is presented in Fig 4. List box and check box tools are widely used.



Сайн байна уу Хонгорзул, та системд нэвтэрлээ.

Fig. 4. 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 of 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 under database menu bar. Fig. 5 presents an example of map interface.



Ground Coordinates - UTM48N
Latitute: 457711.00795118
Longtitute: 4974945.8993804

Site information
Military site type: Уул уурхайн олборлолт
Military site name: Хэрээд

Fig. 5. 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 among 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 user's requirements.

Report output. This 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.

CONCLUSIONS

The database contains 282 contaminated and potential sites with 1550 samples, of which 1363 have been taken from soil and 187 from water. At 365 sampled points, indicators exceeded the permitted value in the soil quality standard MNS 5850. The dominant contaminants in the soil are Hg (39%), As (25%), Zn (3.8%), Cu (3.3%), Pb (2.4%), and Cd (1.4%). The main contaminating reason was gold (65%) and coal mining (10%). The most contaminated areas are located in Bayankhongor (18%) Tuv (16.5%), Govi-Altai (13%) and Uvs (11.5%) aimags. These statistics were generated from the database reports by comparing contaminant values with the standard permitted value, not by investigating sites by researchers and experts in a detail. The water contamination data was not reported because of limited data and data quality.

In the future, detailed field survey works should be conducted regularly, and methodology for contamination and risk assessment should be improved.

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ENVIRONMENTAL POLLUTION ABATEMENT APPROACH - KNOW-HOW TRANSFER PROJECT OF THE CZECH - MONGOLIA DEVELOPMENT COOPERATION

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KEYWORDS
Polluted sites, priority classification, database, methodological guidelines, demonstration investigation

ABSTRACT

The paper describes the project specified in its title. The goal of the project was to strengthen an ability of Mongolian authorities and institutions to cope with the problem of environmental pollution from the past and to establish a base enabling a systematic approach to its progressive abatement. Its follow-up depends on the will and effort of responsible Mongolian authorities as for securing relevant legal and organisation conditions and financial means. An important pre-condition is also strengthening of professional capacities.

INTRODUCTION

Consortium of two Czech companies Dekonta and Geomin carried out a know-how transfer project through the Czech Development Agency in Mongolia during the year 2014.

The goal of the project was to strengthen an ability of Mongolian authorities and institutions to cope with the problem of environmental pollution from the past and to establish a base enabling a systematic approach to its progressive abatement.

A direct Mongolian partner of the project was the Office of the National management Council under the Ministry of Environment and Green Development. There were another subjects cooperating on the projects. The National Environmental Information Centre, regional environmental authorities, University and Academy of Science were among the main of them.

The project activities have had these principal outputs:
- means for standardization of the pollution abatement process
- means for optimization of the pollution abatement process.

MEANS FOR STANDARDIZATION OF THE POLLUTION ABATEMENT PROCESS

Set of methodological guideline documents was developed to support professional approach of Mongolian authorities and institutions.

These guideline documents were developed to cover individual aspects of pollution investigations and interpretation, assessment and exploitation of their results:
- Pollution investigation methodology.
- Principles of representative sampling.
- Sampling methods.
- Risk analysis methodology.
- Geophysical methods in pollution investigation.
- Review of remediation methods.

Rather unexpected difficulties were connected with translation of these documents to Mongolian language. En explanation dictionary had to be also prepared to ease of their use.

Principles of proper professional practice were directly demonstrated to Mongolian professionals and students in the field. Preliminary investigation of 21 polluted sites was executed in the frame of the project. Some details of that topic are treated in further part of this article. A know-how dissemination seminar was organized at the final stage of the project.

MEANS FOR OPTIMISATION OF THE POLLUTION ABATEMENT PROCESS

This part of the project work included these principal activities:

- development of the priority classification system,
- construction of the database of polluted sites.

PRIORITY CLASSIFICATION SYSTEM

Remediation of pollution from the past must be an important component of the state policy on the field of care for human health and environment. Due to large number of such sites, the issue will demand long time and large costs. Under such circumstances, primary attention must be paid to sites representing the biggest and actual threat to human health and environment. To ensure effective allocation of effort and money, some priority classification system must be available.

To be really useful as a supporting toll for decision making, such system must be simple, well-balanced, friendly-to-use and transparent There is a general and understandable reluctance of practice to complex systems with low transparency that are based on classification of large number of parameters of different kind.

The system proposed for Mongolia sorts all polluted sites to three basic categories according to the general character of appropriate further action with respect to character of the impact of an actual or potential pollution to public health and environment:

- sites where remediation is necessary or desirable to mitigate existing or potential site pollution impacts to human health and/or to environment,
- sites with none or insufficient investigation - available information on the site pollution is not sufficient for conclusions concerning necessity, urgency and character of remediation - an investigation (or more detailed investigation) of the site is required,
- sites not requiring any further action (unpolluted or already remedied sites).

There is more subtle classification within each of first two categories with respect to urgency of further action and with respect to existing or estimated size and seriousness of a site pollution impact. Classification of sufficiently investigated sites is derived from conclusions specified in their investigation and risk analysis (or remediation) reports (reflects, is based, issues).

In reality, most sites are still without any investigation, not speaking of sampling. These suspicious (potentially polluted) sites must be classified primarily with respect to urgency of their investigation. Factors entering into the classification algorithm are: character of the present and historical site usage, character of potential pollution receptors and neighbouring land use, number of potentially endangered persons, some basic factors influencing possibilities of pollution spreading.

Similar, but already more specific approach to classification can be applied for insufficiently investigated sites, where at least some sampling was performed although it was not sufficient for a final decision regarding a further action. In case of sites with none or insufficient investigation, a site visit is usually a must to gather information required by the classification system.

DATABASE OF POLLUTED AND POTENTIALLY POLLUTED SITES

The database software system was developed, constructed and tested in the frame of the project of the development co-operation between the Czech Republic and the State of Mongolia in 2014. The system enables to register polluted and potentially polluted sites and also waste water and mine water discharges to rivers and lakes. Thus, it will be possible to exploit the database for the overall management and control of pollution load and for protection of public health and environment within the frame of delimited territorial administration units or watersheds.

The system enables classification of priorities, data sorting and data selection operations and also map presentations from various points of view according to the actual requirements. Priority classification of sites is highly automatic (fully automatic for potentially polluted sites) but always with an offer of "manual" corrections.

Presentation segment of the system is constructed as the web application that can be operated by common web browsers. It enables an access to important segment of environmental information both to authorities and to common public. Also an editing and administration interface of the system is arranged in this way.

Usefulness of the database system for the practice depends on its completeness - ideally it should contain relevant data on all polluted and potentially polluted sites of the whole country. The introductory countrywide inventory would be the most effective way to achieve that goal within a relatively short time. A proposal for its organization was also developed in the frame of the project. Of course, the database must be afterwards continuously extended and up-dated to keep its usefulness permanently.

FIELD INVESTIGATIONS

Preliminary field investigations with sampling were carried out on 21 sites suspected of significant pollution and its potential impacts.

Selection of sites was based on the site identification campaign that was organised by the Office of the National management Council. The campaign was organised in Ulaanbaatar, Central Aimag and aimags Selenge, Darchan, Bulgan, Erdenet, Dornogovi. Regional environmental authorities were appealed to identify sites posing potential priority problems in their regions and to fill in a questionnaire sheet for each such site. That questionnaire contained all parameters enabling a site classification by the system described above (classification software itself was still under construction at that time). It was the first opportunity for testing the priority classification system that confirmed its usability for practice.

The following step were introductory reconnaissance visits of all identified sites. These visits were organised in close cooperation with people from regional environmental authorities and with local environmental inspectors. Visits issued to a final selection of sites for preliminary investigation and were exploited for preparation of sampling plans.

Review of site types that underwent demonstration preliminary investigations during the summer season 2014:
- petroleum handling and storage terminals,
- former army bases,
- wood tar impregnation facilities,
- obsolete pesticide storage and dumping sites,
- livestock disinfection field basins,
- abandoned gold mining sites with sludge pits,
- crude oil exploitation field with waste lagoons and uncontrolled crude oil issues,
- abandoned industrial site - glass factory,
- heat station fly ash lagoons,
- waste sludge outlet from a tanning factory.

The following table presents a review of samples taken for analyses.

Tab.1. Review of samples

Water samples		Solid matrix samples	
Surface water	14	Soil, sludge, waste	162
Groundwater	21	Stream sediments	15
Waste water	4	Construction materials	4
QA/QC	5	QA/QC	24
Total	44	Total	205

Inorganic analyses were carried out in a Mongolia certified laboratory while all samples for analyses of organic compounds had to be sent to the Czech Republic.
Pollution assessment reports together with preliminary risk analyses were developed for all investigated sites.

Six sites were selected as having the most serious potential impact to human health and/or environment and projects for their further detail investigation stage were developed.
Four from these six sites are hoped to undergo a detail investigation as the follow-up of the Czech - Mongolia development cooperation in 2015.

SOME CONCLUDING REMARKS

In spite of its exceptional low population density, Mongolia seems to be no exemption as for the scope of potential threats to human health from environmental pollution from the past. It can be supposed that large portion of polluted sites is located in areas of higher population density because it is closely related to intensity of various economical activities (may be with an exemption of pollution from illegal gold ore processing).

One of priority problems can be a real threat to health of people from inappropriate dumping of pesticides that was a common practice in the past.

A frequent problem looks to be lagoons of fly ash from heating stations that are exposed to wind and that are often located close to residential zones.

In spite of a previous effort, there are still sites with unsecured hazardous wastes from illegal gold ore processing with use of cyanides or mercury.

For sure, some sites with heavy pollution by chlorinated solvents (both from civil and military activities) must be supposed to exist in Mongolia in spite of the fact that they have not been identified as yet. Former Soviet army bases that had been examined in the frame of the project looked not to represent a serious threat to environment.

The project being presented in this lecture could represent a god starting point for systematic approach to old pollution abatement process in Mongolia. Its follow-up depends on the will and effort of responsible Mongolian authorities as for securing relevant legal and organisation conditions and financial means. An important pre-condition is also strengthening of professional capacities. An obstacle is also a non-existence of a laboratory equipped and certified for analyses of organic pollutants in water and soil.

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AFTER 25 YEAR EXPOSURE MODELLING: SIMILAR MODEL STRUCTURES, DIFFERENT EXPOSURES

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INTRODUCTION

A practical possibility for assessing human exposure is that of calculating human exposure, using a so-called exposure model. Such an exposure model enables the calculation of the rate of soil contaminants that enter the human body, blood stream, or target organs. 25 Years ago, the first exposure models were published in the US and in the Netherlands. In the next 25 years, several alternative exposure models have been developed, partly based on existing exposure models. Simultaneously, existing exposure models underwent revisions, mainly in the 1990ties.

Today, several exposure models are worldwide available. These models have a similar basis structure. They consider direct contact with the soil and intake of so-called contact media that include soil-borne contaminants. In its simplest description, they include a series of intake rates of several materials via oral, inhalation and dermal pathways, multiplied by contaminant concentrations in these media, corrected for different absorption processes in the human body and normalized according to body weight. Since contaminants enter the body via the mouth, nose or skin (external exposure), the absorption in specific organs has to be specified. Moreover, exposure models include three elements: (1) contaminant distribution over the soil phases; (2) contaminant transfer from (the different phases of) the soil into contact media; and (3) direct and indirect exposure to humans. From a survey focused on the state of the art in the European Union it was concluded that the most important exposure pathways are exposure through soil ingestion (including soil-borne dust), vegetable consumption and vapour inhalation (Carlon and Swartjes, 2007).

Input parameters used in different exposure models, however, do differ substantially. Differences between input parameters in different models increase in the order: compound-specific properties; human characteristics; parameters that describe physico-chemical processes; human behaviour factors; geological factors (soil/water); climatic/ cultural factors (Swartjes, 2015). In this paper, the differences in input parameters have been illustrated.

MAJOR EXPOSURE PATHWAYS

Exposure through soil ingestion

The combined soil and dust ingestion rates have been determined mainly by tracer studies, using typical soil constituents as aluminium, silicon, titanium, and yttrium in faeces and urine as indicator (e.g., Stanek et al., 2001). From these tracer studies, combined soil and dust intake rates range from 31 – 195 mg/day (Bierkens et al., 2011). From these studies, using measurements from the period 1986-1997, 100 mg/day seems a reasonable estimate as central tendency estimate. However, since the behaviour of children regarding time use, including time spent outdoors, changed considerable the last two decades, this figure could be an overestimation today. For adults, combined dust and soil intake rates are from 23 - 92 mg/day (Bierkens et al., 2011). In some models and model applications, ingestion rates outdoors vary with land use, e.g., lower for residential land use without garden, since for this land use only a minor part is unpaved and the possibility for gardening is lacking. For specific human health risk assessments, sometimes extreme soil ingestion rates are taken into consideration. In case of the consideration of children showing pica behaviour[1] soil ingestion rates as high as 1,000 mg/day are used and in case geophagy[2] is considered, values up to 50,000 mg/day are used (US Environmental Protection Agency, 2011).

In some cases, it is useful to make a differentiation between soil and (soil-borne) dust ingestion. First, crawling children are in intensive contact with floor dust. Second, soil particles in dust generally are finer than soil particles outside, which might lead to enrichment of contaminants. The fraction of soil in house dust ranges

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[1] Pica is an eating disorder, mostly by children, characterized by an appetite for non-nutritive materials, including soils, which is not part of any cultural practice

[2] Geophagy is the culturally driven practice of eating soil materials, most often in rural or preindustrial societies in Africa and Asia, in particular among children and pregnant women, partly as nutrient supplement

between 0.20 and 0.80 and could be considered land use-specific. In a few model approaches, contaminant enrichment in the <50 μm particle size fraction with a factor up to five is implemented (Juhasz et al., 2011). Another factor that differs between models is the fraction that is supposed to adhere to the hands (Siciliano et al., 2009).

Another factor that is in some cases considered, but is most cases is neglected, is the contaminant-specific relative bioavailability factor in the human body (Cave et al., 2011). This factor is used for metals to cover the difference between intake (external exposure) and uptake (internal exposure) after soil ingestion. The best model currently available to estimate the bioavailability is the Unified BARGE method (UBM; Wragg et al., 2009), developed by the Bioaccessibility Research Group of Europe (BARGE) (BARGE, 2015). In rare studies, risks from soil ingestion are determined in more detail through subdivision of the different factors that control the exposure through soil ingestion. In that case separate factors for hand dust cover, the transfer from hand to mouth, hand mouth contact frequency, the surface of thumb, palm and the upper part of the three middle fingers and relative bioavailability are used.

Exposure through vegetable consumption

For the fraction of vegetables that is homegrown, no decent statistics are available and different numbers are used. Selected values are often based on a policy decision: 'the soil quality must offer the possibility to consume a specific percentage of vegetables from one's own (vegetable) garden'. The most challenging aspect of the calculation of exposure through vegetable consumption is the determination of the accumulated concentration in vegetables, at the moment of harvesting. In the majority of the exposure models a generic bioconcentration factor (BCF), i.e., the ratio between the concentration in plant and in soil, for all vegetables and independent on soil concentration and soil properties, is used. Given the different uptake properties of vegetables, a rather large variation is expected. The BCFs for copper from the RIVM dataset (n= 46 paired vegetable and soil concentrations; Swartjes et al., 2007), however, range from 0.07 up to 1.01. Since the relation between soil and vegetable concentrations is generally curvilinear, plant uptake is overestimated at higher soil concentrations when a generic BCF is used.

In several model approaches a more sophisticated way to predict the metal concentration in vegetables is based on empirical Freundlich-type relations. In these relations, the accumulated concentration in vegetables is calculated as a function of the concentration in soil and the soil properties such as pH, organic matter and clay contents. Subsequently, a consumption-weighted concentration in vegetables can be calculated, accounting for an average accumulation in different vegetables and the actual soil properties. Analogously, several models include a more sophisticated procedure to calculate the uptake op inorganic contaminants (Trapp and Legind, 2011). In this model, the accumulated concentration of organic contaminants in roots at equilibrium is calculated based on the concentration in soil, the transpiration rate, the root mass, its first order growth rate, and the partition coefficients between root and water and water and soil. In a subsequent step, the accumulated concentration of organic contaminants in the leaves at equilibrium is calculated from the concentration of organic contaminants in the roots. In principle, the root uptake in vegetables could be calculated on a mechanistic basis, including three subsequent processes, i.e., speciation in soil, plant root uptake and transport within the plant. Given the large uncertainties in the calculation of all three processes, and hence the limited reliable estimates of the accumulated concentration in vegetables, this procedure in not yet followed in any exposure model.

Exposure through indoor air inhalation

The most challenging aspect of the assessment of exposure through indoor air inhalation is the determination of the indoor air concentration. Basically, two options are used for calculating the indoor air concentration, i.e., using standardised empirical attenuation factors (e.g., US Environmental Protection Agency, 2012) or using a vapour intrusion model. These vapour intrusion models include four processes that determine the indoor air concentration, using the groundwater concentration as starting point. These processes are: (1) convection and diffusion in groundwater and soil; (2) intrusion into buildings; (3) ventilation; and (4). degradation during the whole pathway from soil or groundwater to indoor air. The four mentioned processes above are difficult to quantify and it is generally recognized that this pathway is a weak element in human health risk assessment.

Provoost et al. (2009) performed a validation study on vapour intrusion models, including eight exposure models. It was concluded that, although in some cases the models predict too low concentrations, the models have a tendency to overestimate the indoor air concentrations. A plausible explanation of the overestimation of the models could be that degradation processes are not included in the models (e.g., Picone et al., 2012). The differences between predicted and measured indoor air concentrations were the highest at low indoor air concentrations. At indoor air concentration higher than 1 $\mu g/m^3$ the differences between predicted and measured indoor air concentrations were generally within three orders of magnitude.

Exposure through other pathways

Except for the three major exposure pathways described above, other pathways may be of importance in specific situations. Volatile contaminants and metals have minimal potential for dermal uptake due to the likelihood that they will volatilize faster than dermal uptake could occur and a low tendency to partition into skin lipids, respectively. Critical input parameters for estimating dermal uptake from soil include dermal absorption fractions, skin adherence factors, and skin surface area exposed (Elert et al., 2011).

In particular cases, exposure through the inhalation of soil-borne particulate matter can be of importance, in particular in areas with favourable wind conditions (bare and open surfaces, limited vegetation) and high soil concentrations. The latter conditions might prevail around (former) mining areas. For the inhalation pathway, the fraction of dust particles smaller than 10 µm (PM10) is the most relevant fraction (Knol and Staatsen, 2005), but different fractions are considered in exposure models.

EXPOSURE MODEL COMPARISON

For gaining insight in the variation in calculated human exposures due to soil contamination, Swartjes (2007) investigated the variation in calculated exposures (total exposure and exposures along the separate exposure pathways). Exposure calculation for 40 hypothetical exposure scenarios were carried out using seven exposure models; the models are Cetox-human (DK), CLEA (UK), CSOIL (NL), ROME (IT), VlierHumaan (Flanders, BE) and two models without name from France and Sweden. The 40 scenarios are defined by a combination of four factors, i.e., (1) type of contaminant (atrazine, benzene, benzo(a)pyrene (B(a)P), cadmium (Cd), or trichloroethylene (TCE)); (2) soil type (clay or sand); (3) land use (residential or industrial land use); and (4) selection of input parameters (standardised or model-specific input parameters) (for details see Swartjes, 2007). The concentrations of the contaminants were put equal to the Dutch Intervention Values. It was concluded that the use of different models could lead to quite different exposures for the same exposure scenarios. This is illustrated in Fig. 1, in which the calculated exposures for four scenarios are shown, as an example, using the seven different exposure models. For these scenarios, the ratio between the highest and lowest calculated total exposure (exposure along all exposure pathways combined) using the seven exposure models ranged from a factor of 149 (TCE, industrial land use, clay soil, model-specific input parameters) and 1235 (B(a)P, residential land use, sandy soil, standardized input parameters).

For better understanding the variation in calculated human exposures due to soil contamination, Swartjes (2009) compared the variation in calculated exposures with the variation in calculated concentrations in contact media and in the soil compartments, along with the variation in the input parameters using the same exposure model calculations according to the 40 exposure scenarios as described above. This led to the conclusion that most of the variation in exposure through soil ingestion could be explained by differences in the input parameter average daily soil intake. When model-specific input parameters were used, the variation in exposure through vegetable consumption could be explained by differences in the product of total consumption rate and fraction of total consumption rate that is home-grown. When standardized input parameters were used, this variation was comparable to the variation in concentration in root vegetables and in the concentration in leafy vegetables. The variation in exposure through indoor air inhalation was comparable to the variation in concentration in indoor air. This suggests that the parameters that control the variation in concentration in the indoor air, that is, surface and volume of the building and, to a lesser extent, ventilation frequency of the building, also control the variation in exposure through indoor air inhalation.

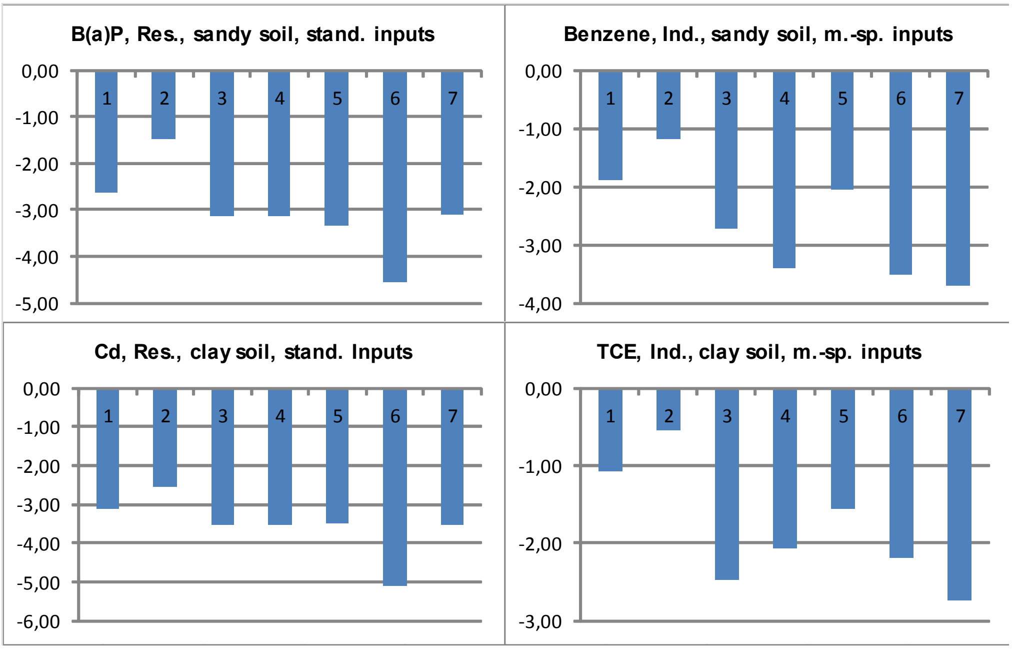

Fig. 1. Calculated exposures (mg. kg_{BW}^{-1}. day^{-1}; log-transformed) for four scenarios, using seven different models (models 1 to 7 in arbitrary order)
Res. = Residential land use; Ind. = industrial land use; stand. inputs = standardized input parameters; m.-sp. inputs = model-specific input parameters

HARMONISATION

The diversity in input parameters in exposure models is partly explained by different geographical, cultural and social conditions, and sometimes due to differences in policy choices. However, lack of scientific consensus also explains an important part of the differences. One of the major challenges in human health risk assessment today is to move towards more consistency in the risk assessment tools used by the European Union member states (Swartjes et al., 2009) or, even better, worldwide. A stronger convergence of risk assessment tools would contribute to scientific integrity, a level playing field and a higher perception of justice among stakeholders. To this purpose, human health-related risk assessment tools that do not include geographical, cultural, social or policy elements should be standardised (*standardised* risk assessment tools). For risk assessment tools that do include geographical, cultural, social or policy elements, a protocol must be developed allowing a certain level of flexibility so as to account for these elements (*flexible* risks assessment tools).

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S-RISK – A FLEXIBLE MODEL FOR HUMAN HEALTH RISK ASSESSMENT AT CONTAMINATED SITES

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KEYWORDS
Contaminated sites, environmental impact assessment, groundwater remediation, human health risk assessment, online web application, soil remediation, S-Risk

ABSTRACT

Background
In 1995, the region of Flanders (Belgium) set forth its first Flemish Decree on Soil Remediation, outlining policies for soil remediation in the region. To empower its implementation, a software model for the calculation of soil remediation values and human health risks was developed. This model – Vlier-Humaan – was based on the state-of-the-art scientific models available at that time. Over the years, however, exposure and risk assessment science significantly progressed and a revision of the model became indispensable. In 2008, a revision document was finalized describing the framework, equations and parameterization of a new model named “S-Risk” (Cornelis et al., 2008). This model was further developed (Cornelis et al., 2013) and implemented in the form of an online web application, which was made publicly available in June 2013. Since October 2013, S-Risk is the official reference model for human health risk assessment at contaminated sites in Flanders (OVAM, 2013).

Model description
S-Risk enables the calculation of generic or site-specific human health-based screening levels as well as the prediction of human health risks from a contaminated site. It can deal with both organic and inorganic chemicals. The environmental fate and distribution of these chemicals are calculated according to steady-state conservation of mass principles. S-Risk combines four main model systems:

- distribution of the chemical within the soil compartment;
- transfer from soil and groundwater to other environmental and biological compartments;
- human exposure from the different environmental and biological compartments;
- human health risk following from the calculated exposures.

Module 1 calculates the distribution of the chemical over solid, water and gas phases of the soil compartment. For the groundwater compartment, distribution between water and gas phase is calculated at the boundary between groundwater layer and unsaturated zone, by assuming equilibrium partitioning. Concentrations in the soil water phase in the unsaturated zone are limited by the solubility of the chemical.

Module 2 considers the following transfer pathways (see also Figure 1; pathways are indicated in blue and green):
transfer from surface and subsurface soil layers to outdoor air by volatilization;

- transfer from surface and subsurface soil layers to indoor air by volatilization (vapor intrusion);
- transfer from surface soil to outdoor air and indoor air by soil resuspension;
- transfer from surface soil to indoor settled dust;
- transfer from surface soil to vegetation by root uptake and translocation;
- transfer from surface soil to above-ground vegetation by soil splash;
- transfer from outdoor air to vegetation by gas-exchange and particle deposition;
- transfer from soil to drinking-water by permeation through plastic drinking-water pipes;
- transfer from groundwater to outdoor air by volatilization;
- transfer from groundwater to indoor air by volatilization (vapor intrusion);
- transfer from soil to groundwater by leaching;
- transfer from drinking-water to bathroom air by volatilization;

- transfer from soil, water and feed to meat, milk and eggs by exposure of cattle and chicken (feed, soil and water intake).

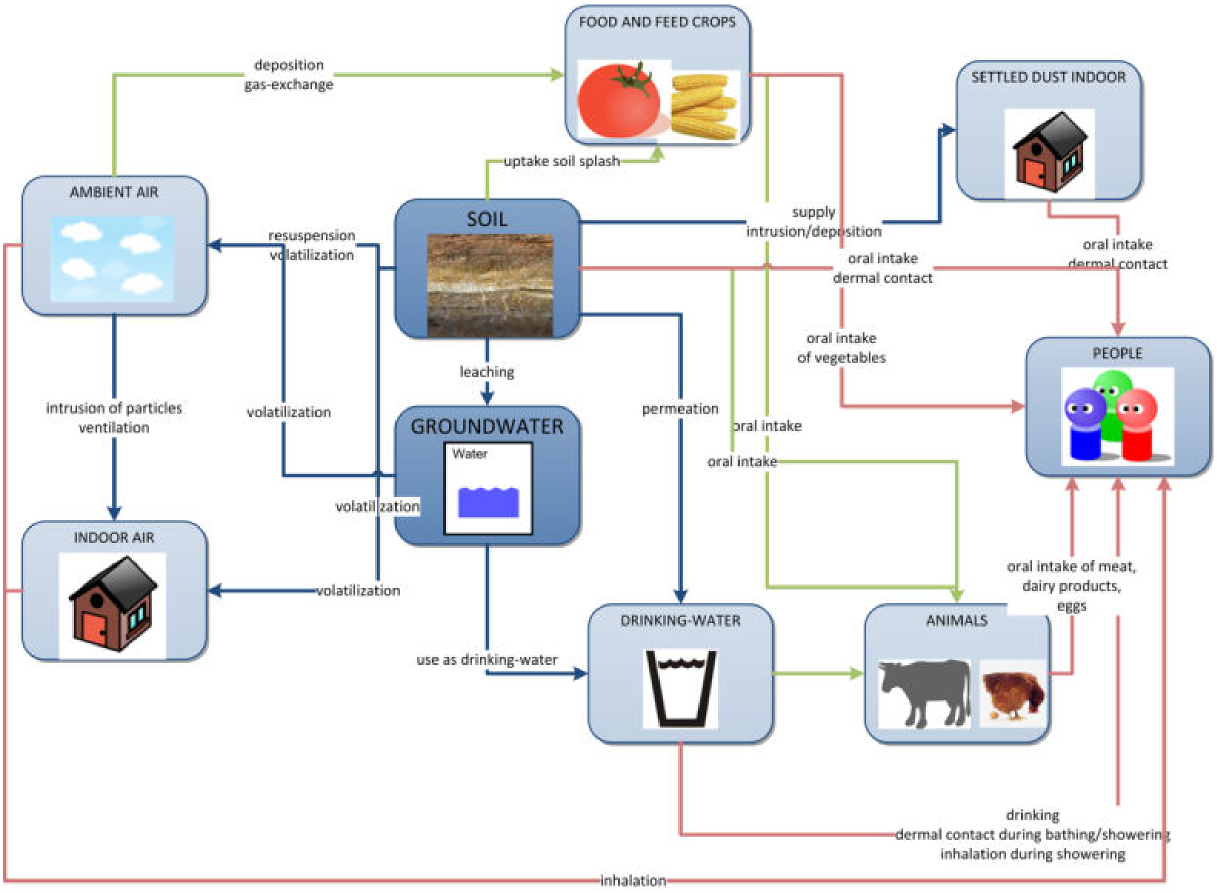


Fig. 1. Schematic overview of the different transfer pathways and exposure routes considered in the S-Risk model

Based on user-specified soil and optionally groundwater concentrations, the transfer calculations in Module 3 result in chemical concentrations in ambient air, indoor air, drinking-water, settled indoor dust and food products (i.e., vegetables, meat, dairy products and eggs). Subsequently, these concentrations are used to predict human exposure via the following exposure routes (see also Figure 1; routes are indicated in red):

- oral exposure:
    - intake of soil and indoor settled dust particles;
    - intake of vegetables;
    - intake of animal products (i.e., meat, milk and eggs);
    - intake of water (i.e., drinking-water and/or ground water);
- inhalation exposure:
    - inhalation of outdoor and indoor vapor phase contaminants;
    - inhalation of outdoor and indoor particle phase contaminants;
    - inhalation of vapor during showering;
- dermal exposure:
    - absorption from soil and settled dust particles;
    - absorption from water during bathing and showering.

Exposure is calculated for a set of predefined age classes starting at age 1 to > 70 year.

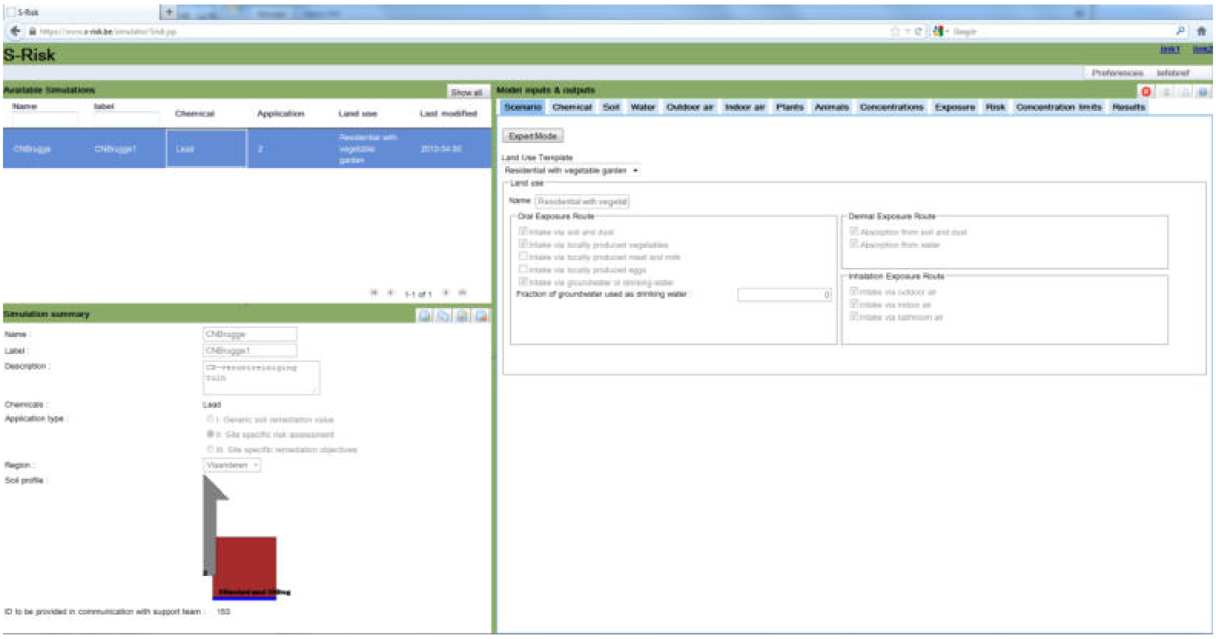
In Module 4, human health risks are calculated by comparing the calculated exposure dose (for oral and dermal routes) and exposure concentration (for the inhalatory route) to toxicological reference values. How exactly the exposures from the three different exposure routes are combined, depends on the toxicological characteristics of the chemical compound (i.e., threshold *vs.* non-threshold and local *vs.* systemic health effects) and can be specified by the user. Toxicological reference values can be differentiated by age class. To complete the risk assessment, in a parallel step, the concentrations in the environmental compartments are compared to legal or toxicological limits.

The modelling framework of S-Risk is implemented in Matlab® (The Mathworks, Inc., Natick, Massachusetts, USA), interfacing with a Java/Spring based web front-end. The simulation data are stored in a relational MySQL™ database (Oracle Corporation, Redwood Shores, California, USA).

Use of the online web tool

S-Risk is available as a web application for registered users at https://www.s-risk.be (see Figure 2 for a screenshot of the S-Risk main interface). It enables the flexible creation of model scenarios, easy management of user simulations and the generation of detailed reports. Once logged in, the user interface of the S-Risk model allows to choose between three main application domains (see also left, at the bottom of Figure 2):

- application I: calculation of generic human health based soil remediation values as required within the legal framework in Flanders, or as a first screening tool for local site risk assessment;
- application II: calculation of site-specific human health risks in the context of a detailed site assessment;
- application III: calculation of site-specific remediation objectives.



Name	label	Chemical	Application	Land use	Last modified
CNBrugge	CNBrugge1	Lead	2	Residential with vegetable garden	2013-04-30

Name : CNBrugge
Label : CNBrugge1
Chemicals : Lead
Application type :
○ I. Generic soil remediation value
● II. Site specific risk assessment
○ III. Site specific remediation objectives
Region : Vlaanderen
Soil profile :
ID to be provided in communication with support team : 153

Land Use Template: Residential with vegetable garden
Land use
Name: Residential with vegetal
Oral Exposure Route
☑ Intake via soil and dust
☑ Intake via locally produced vegetables
☐ Intake via locally produced meat and milk
☐ Intake via locally produced eggs
☑ Intake via groundwater or drinking water
Fraction of groundwater used as drinking water: 0
Dermal Exposure Route
☑ Absorption from soil and dust
☑ Absorption from water
Inhalation Exposure Route
☑ Intake via outdoor air
☑ Intake via indoor air
☑ Intake via bathroom air

Fig. 2. Screenshot of the S-Risk overview page

After choosing the appropriate application domain, the relevant land uses (i.e., a land use type with corresponding exposure routes and parameters) for the site under consideration is selected. By default, nine different scenarios are available in S-Risk (see also on the right side of Figure 2):

- agricultural;
- residential:
    - with vegetable garden;
    - with garden;
    - without garden;
- recreational:
    - day recreation mainly outdoors (incl. sport);
    - day recreation mainly indoors (incl. sport);
    - holiday resort;
- industrial:
    - light industry (i.e., offices, shops, etc.);
    - heavy industry.

Simulations can be performed using these default scenarios, but also by defining new ones based on the built-in scenario types.

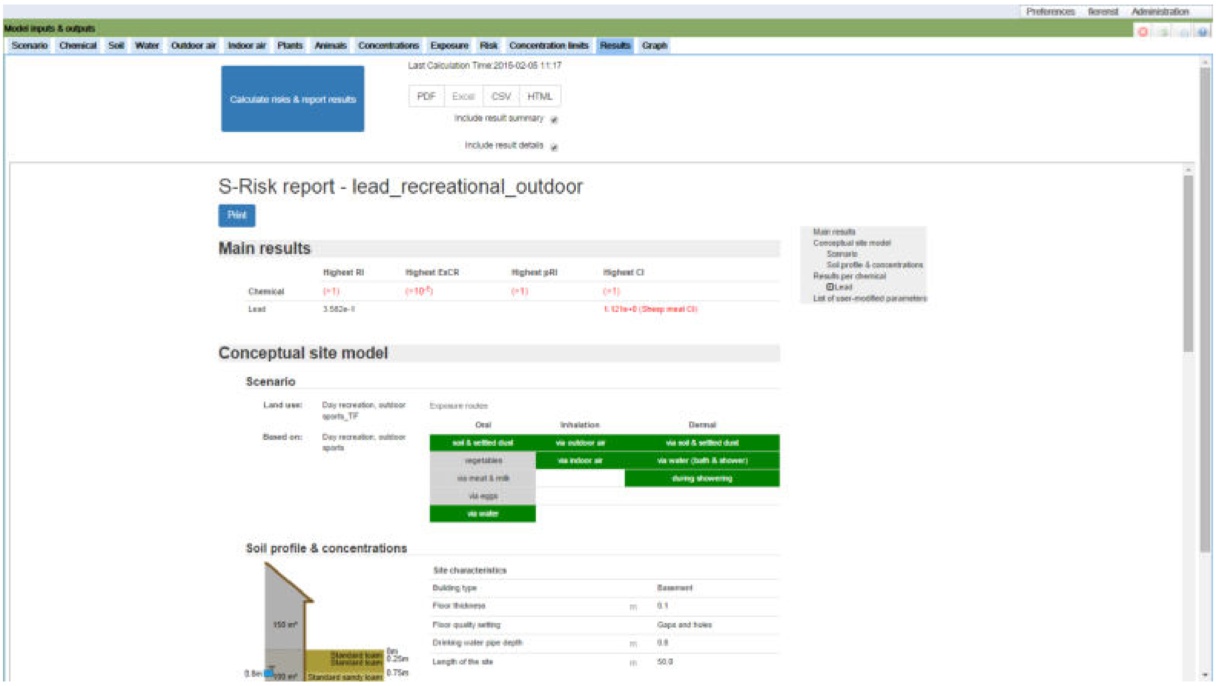
Subsequently, contaminants and their properties need to be provided. S-Risk offers a database of about 80 built-in chemicals. This list contains chemicals for which Flemish soil remediation values are available or chemicals that have been part of documents in preparation of soil remediation values. Among others, it covers heavy metals, BTEXs, chlorinated compounds and total petroleum hydrocarbon fractions. Chemical properties can be modified by the user. Alternatively, new chemicals can be manually added to S-Risk as well. Simulations can be run for more than one chemical at the same time.

A flexible soil profile (i.e., with multiple soil layers) can be specified in full detail. Soil properties and concentrations for all selected contaminants need to be filled in layer by layer, allowing a combination of selecting built-in soil types and user-defined values. Optionally, separate soil concentration profiles can be entered for indoor and outdoor volatilization calculations. In contrast to the soil layers, concentrations in groundwater can be either user-specified or predicted by a simple on-site dilution model available in S-Risk. With respect to the indoor environment, S-Risk considers three building types: a building without a basement (i.e., slab-on-grade), with a basement or with a crawl space.

At any time, modeled intermediate concentrations in the various environmental compartments can be overruled by user-provided measured values. Risk thresholds and toxicological reference values can also be flexibly defined for varying age groups.

Once all data are entered, simulation calculations can be started. A quick overview of the simulation results can be consulted on the Results page (see Figure 3 for a screenshot); a more detailed report can be downloaded in PDF, Excel, CSV or HTML formats. Simulation configurations and results are stored securely on the S-Risk server, so they can be accessed from any web-enabled computer.

Although a number of chemicals, scenarios and specific data sets are available as “defaults” and inspired by the Flemish context, they can be adapted on a per-simulation basis. Moreover, S-Risk’s flexibility and open structure allows for customization of the model for other regions in Europe as well. This includes the use of country specific parameters and/or risk evaluation frameworks.



Last Calculation Time:2015-02-05 11:17

S-Risk report - lead_recreational_outdoor

Main results

	Highest RI	Highest ExCR	Highest pRI	Highest CI
Chemical	(<1)	(<10⁻⁵)	(<1)	(<1)
Lead	3.582e-1			1.121e+0 (Sheep meat CI)

Conceptual site model

Scenario

Land use: Day recreation, outdoor sports_TF

Based on: Day recreation, outdoor sports

Soil profile & concentrations

Site characteristics

Building type		Basement
Floor thickness	m	0.1
Floor quality setting		Gaps and holes
Drinking water pipe depth	m	0.8
Length of the site	m	50.0

Fig. 3. Screenshot of the S-Risk Results page

Additional information
More information concerning the use of the S-Risk model and the modelling framework can be found on the S-Risk web page (https://www.s-risk.be/documents). Questions (e.g., demo license requests and licensing information) can be asked via the S-Risk online contact form (https://www.s-risk.be/contact) or via e-mail at info@s-risk.be.

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THE USE OF GEOPHYSICAL METHODS WHILE ASSESSING THE EFFECTS ON ENVIROMENTAL BURDENS

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KEYWORDS
Geophysical methods, environmental impact assessment, monitoring of environmental impacts, contaminated sites, contaminant, environmental burdens

ABSTRACT

The aim of the presentation is to assess the possibilities of use of the geophysical methods while examing the impact of environmental burdens on the environment with practical examples. This is derived from the results of geophysical measurements on the task - a project of the Ministry of Environment (MoE): "Monitoring of environmental impacts on geological environmental factors in selected regions of the Western Carpathians" and the "Monitoring of environmental exposure of selected areas of the Slovak Republic", which focuses on assessment of the impact burdens on geological environmental factors.

OVERVIEW

This article is focused on assessing the possibility of using geophysical methods in the examination of the impact of environmental burdens. Based on the results of geophysical surveys on the role of "Monitoring of environmental burdens in selected locations in the Slovak Republic" Part VI. Geophysical surveying services for the project: "Monitoring of environmental burdens in selected locations in the Slovak Republic" and "Monitoring of environmental impacts on geological environmental factors in selected regions of the Western Carpathians " (2000-2005).

The methodology geophysical methods use, particularly widely applied geoelectrical methods in hydrogeological survey and the prospecting ecological burden is fairly well defined. (Karous, M.,1998). A good source of information when choosing methodologies were methodological guide of the Ministry of Environment of the Czech Republic from 2009: "Possibilities of geophysical methods in verifying vague geological, possibly other relations in the localities in the exploration and remediation of old environmental burdens " .

SURVEY METHODOLOGY

During the implementation of works we have approved following procedure:

- Detailed archives exertion of all available related documents and information
- On-site reconnaissance to determine the general conditions for upcoming geophysical surveying
- General screening of physical parameters. For screening we used all available information regards the change of physical parameters (thermo parameters, resistivity, etc.)

The most used method was the **resistivity surveying**, where we measured the changes in apparent resistivity or apparent conductivity of the environment, in regards to changes in geological properties of the environment.

General aspect for conducting the resistivity methods for the assessment of the environmental impacts is that the resistivity of the ground is closely related to water content and its mineralization. Most of the soluble contaminants in the ground water is the electrolyte with significantly different (lower) resistivity, due to a difference in ion concentration. Such contamination is usually well detectable using resistivity methods in the form of conductive anomalies.

As an example we show the comparison of the conductivity and chloride content (Cl) at the Šulekovo site. By Examine of approx. 500 pairs at the laboratory we proved very good correlation between them. (Putiška, R., 2002). This is shown on figure 2.

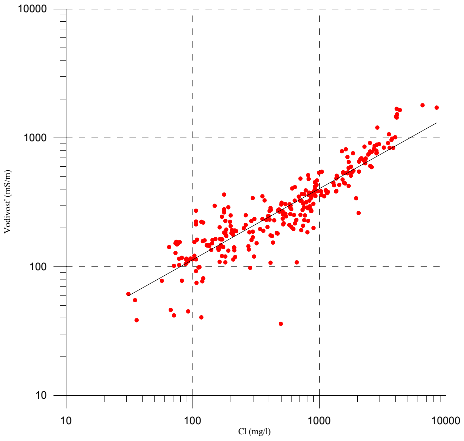


Fig. 1. Correlation of conductivity and Cl content in groundwater around the landfill determined by sampling carried out in 1994, 1998, 1999, 2000, 2001, 2002.

At general screening a dipole electromagnetic conductivity survey (DEMP) of geology environment was very successful, which has given us the basic information on the lithology and basic spatial parameters of the environmental burdens.

Based on the results of the initial surveys, the actual sites were chosen where we conducted other geophysical methods in a more detailed scheme, in both vertical and horizontal direction.

Very good results were also obtained by using resistivity tomography (MES ERT). It is a system of complex resistivity surveying using larger amount of electrodes and a computer controlling the current transmittion and receiving voltage. This method allows us to obtain very detailed picture of the apparent resistivity distribution in a vertical cross section parallel to the survey line. By further analyses the measured data are transformed into an actual resistivity values and through this we obtained a picture of the real structure of the investigated geological environment. Repeating measurements at variable times under suitable conditions enable us also to capture changes in investigating environment and assess the time evolution of the impact of various factors on the environment.

From the other geophysical methods we applied magnetometry, ground penetrating radar (GPR), spontaneous polarization method (SP) and also method of the body charge. Very good results were obtained by the SP in the measurement of different types of leakage, damage, detailed measurements of the integrity of sealing walls, etc. It is a method focused at monitoring existing natural stationary electric fields produced by the movement of water (ions) in the geological environment.

DATA ANALYSES AND PROCESSING

Geophysical methods were within the major task used in a large number of minor sites. When we were processing the data we have also evaluated the knowledge of geophysics results at other similar sites. It has been shown that their use in solving problems related to the environmental burden requires different methodology of field works and also the way of processing. It is necessary to mention that environmental burdens in accordance with the law (environmental burden - its impact on the environment) requires solution of two other sub-issues:

- Environment burden boundary description
- Assessment of its effects, which are changing in time, dynamic and highly subject to other influences

The current use of geophysical exploration has proven that analyses of acquired geophysical data should be based on the model of contaminants disposition around the burdens (Selects, et al., 2005)

The core of these models is the fact that majority of soluble contaminants form in groundwater electrolyte with very low resistivity, due to the higher concentration of ions. To monitor the subsequent spread of contaminants is necessary to understand the hydrogeological conditions at the site (Christiansen, TH., et al., 2000, Vybíral, V., et al., 2005, Mikita, S., 2010).

It turns out that the general model, in form of contamination cloud, is for spreading of contaminants in saturation of environment very simplified. It is not sufficient to characterize signs of contamination emerging in real environmental conditions. Therefore for need of assess the situation at individual sites, it was suitable to divide the general model into several detailed types (Selects, et al., 2005, Mikita, S., 2010). The main criterion for the division was the location of impermeable layers relative to the burden.

We have allocated 5 main groups – concept models:
MODEL A with zero thickness of overlying layers over the impermeable bedrock - the spread of contaminants takes place on the surface (mainly due to low permeable rock environment and also bigger slopes (Figure 2). Unofficial name is "valley type".

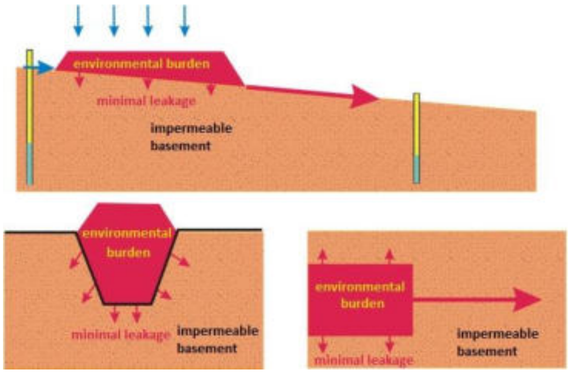


Fig. 2. Model A – burden with zero depth of impermeable layer; a) model cross section; b) front view; c) top view

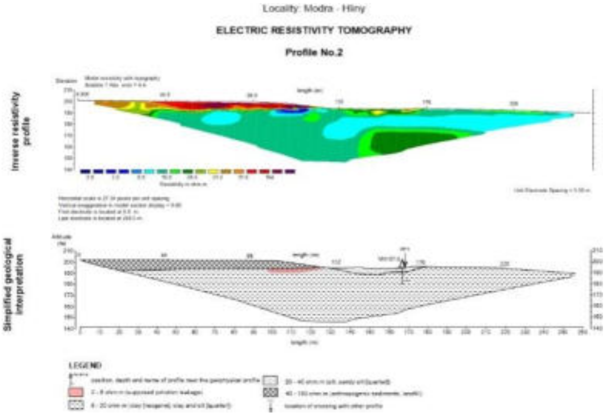


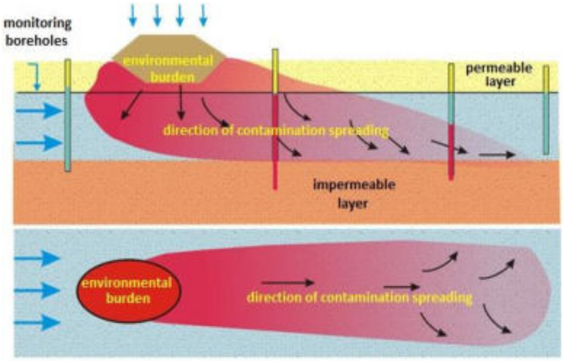
Fig. 3. ERT geophysical survey results at Modra-Hliny landfill

This model is typical for environmental burdens incurred by inducing the waste material into the valley, or into the excavation pits after mining of raw materials. Geophysical operations are concentrated in the foreland of the landfill.

Example site: "Modra - Hliny - landfill with OP", which was created by filling up the empty pit after extraction of brick clay.
FIG. 3 shows a typical inverse resistivity cross section and simplified geophysical and geological cross section of the profile PF2 at this site. Landfill body is represented by higher apparent resistivity (red color) and impermeable basement by low apparent resistivity (light blue – green color). The contamination, which flows at the lowest point of the former mining pit results in minimal apparent resistivity (dark blue)

Model B, in which the burden is placed at the bottom of the river, typically with presents of permeable layer (e.g. quaternary) lying on an impermeable subsoil (e.g. Neogene). unofficial name "alluvial type". Spreading of the contamination is carried out in form of the contamination cloud in the saturation zone, which is limited to a depth boundary (typically within 10-15 m) (Fig. 4). The direction of the contamination disposition is strongly influenced by hydrogeological and hydrological conditions in this area (eg. The variation in levels in nearby rivers). Geophysical exploration in this type is focused on mapping of the preferred location of possible contamination leakage (ie. Monitoring zones). It's necessary to monitor whole landfill area because the direction of the spread of contamination is subject to hydro activity at nearby river.

This model has been studied in detail at sites in the valley of the Vah. The typical example site is "Sered - Nickel smelter - landfill Luzenec". Created was during the operation of nickel smelter in Sered. Fig. 5 shows the typical inverse resistivity cross section and simplified geophysical and geological cross section profile PF11 on this site. Layer of aquifer gravel and sand of thickness of 10 m is represented by higher apparent resistivity (red color) and impermeable bedrock by low resistivity (blue color). Contamination that comes from the Luzenca landfill decreases the resistivity of gravel and is manifested by lower resistivity (green color).



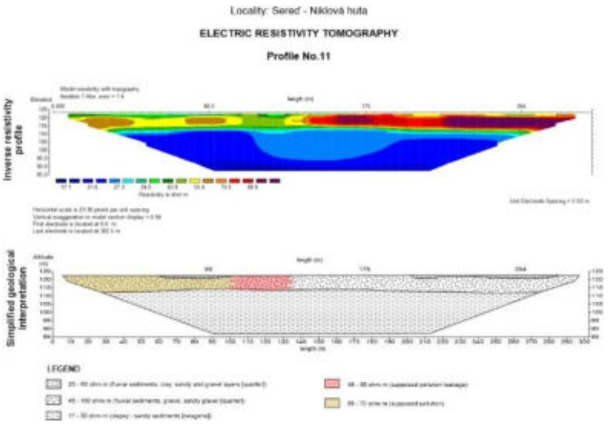
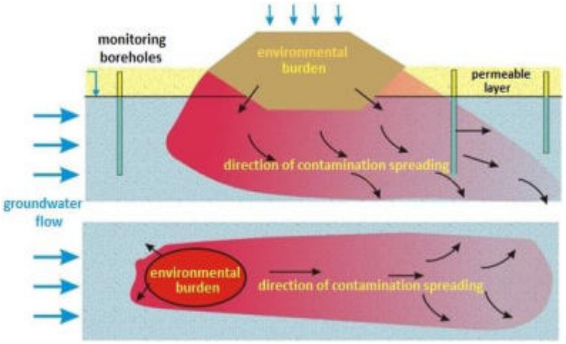


Fig. 4. Model B – the burden with nearby impermeable layer

Fig. 5. ERT geophysical survey results at "landfill Luzenec" Sered

The model without impermeable subgrade (impervious layer is deeper than 10-15 m). We have an evidence was monitored in Slovakia and abroad, in areas with great thickness of porous materials, where burdens incurred after depression formed from gravel mining was filled with domestic waste - Dunajska Streda, Sladkovicovo, Zlate Klasy, that the spread of contamination flows below the landfill body as a result of its higher density (Fig. 6).



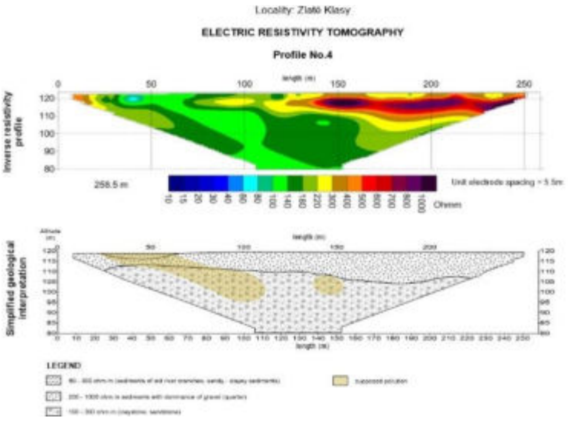


Fig. 6. Model C – burdens located in permeable layer with impermeable subgrade at great depth

Fig. 7. ERT geophysical survey results at Zlate Klasy municipal landfill

Geophysical surveys are concentrated in the near vicinity of the burden to rule out the presents of possible leakage locations. This model is typical for the site: "Zlate Klasy – municipal landfill". This burden has been created by filling up the depression with waste after gravel extraction on site. On Fig. 7 the typical inverse resistivity cross section is shown and simplified geophysical - geological profile PF4 cross section on site. Layer of aquifer gravel and sand of thickness of 10 m is represented by higher apparent resistivity (red color) smoothly continues to deeper sandy locations (green color). Contamination which comes from the landfill represented by low resistivity (light blue color) reduces the apparent resistivity around the landfill and continues to deeper subgrade (light green).

Model of environmental burdens in the vicinity of landfills, closed up by underground sealing walls (USW). Contamination may result from the period before the construction of the USW, or spreads throughout the leaks in USW or in subgrade of the landfill body. Spreading of the contamination cloud in near vicinity of the landfill is conditioned by the same factors as in model B (contaminants from the period before the construction) or C (contaminant through the bottom of landfills) (Fig. 8).

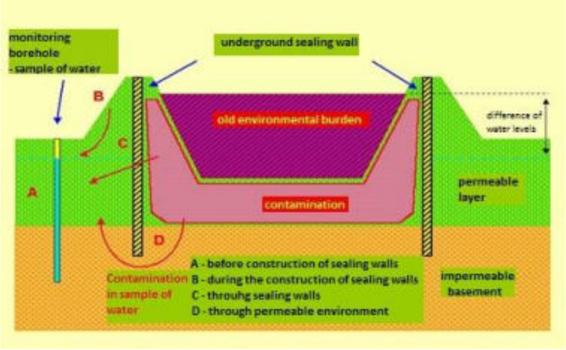


Fig. 8. Model of possible origin of the contamination in the vicinity of the landfill's USW

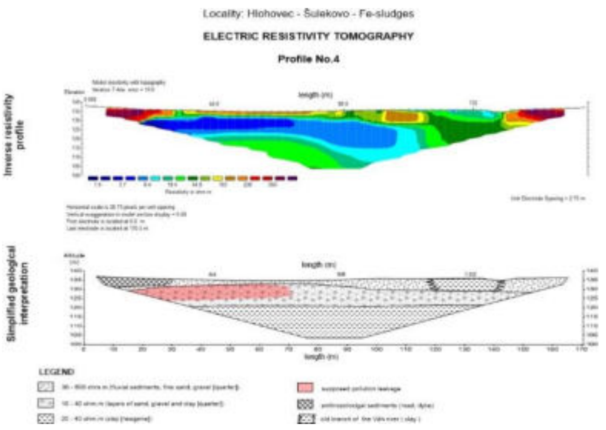


Fig. 9. ERT geophysical survey results at Hlohovec-Sulekovo – Fe sludge

This model is a typical for site: "Hlohovec - Šulekovo - Fe - sludge". Industrial waste is sealed with sealing walls embedded in the impermeable subgrade. Environmental burden represents the contamination formatted at a time before the construction of USW. Approximately 10 years after the closure of the contaminating material using USW, the enclosed contamination has leaked beneath the USW through the sandy layers. FIG. 9 shows the typical inverse cross section of apparent resistivity and simplified geophysical and geological cross section profile PF4 on site. Layer of aquifer gravel and sand of thickness of 10 m is represented by higher apparent resistivity (red color). Contamination which is present under the burden in direction of the underground water flow is represented by low apparent resistivity (blue color).

The fifth model is the burdens in which underground water is in depths greater than 30m and there is no direct connection with the landfill material. Geophysical methods do not follow the processes of contamination, but rather possible changes in the construction of landfill body (dams).

CONCLUSION

A surveying of an environmental burdens from the view of the complexity of the processes going on monitored sites is generally difficult. It's necessary to capture all the changes that are taking place not only in space but also in time. It turned out that the geophysical methods have irreplaceable role in identifying the burdens.

Suitable methods for monitoring of the burdens are the geoelectrical resistivity methods. With their help, under appropriate conditions it's possible to set the border parameters of its own ecological burdens, mapping the spread of the contamination and with repeated measurements also changes taking place in time and space. In some cases it is appropriate to extend the used geophysical methods of magnetometry, spontaneous polarization, GPR, seismic engineering.

Considering the complexity of the processes influencing the processes taking place in and around the burdens, it is advisable to rely on the models showing possible spread of contaminants in the environment and based on them to choose the most appropriate methodology for the survey, monitoring and subsequent remediation and reclamation works.

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ASSESSMENT AND MANAGEMENT OF CONTAMINATED SITES IN FLOOD DISASTER IN SERBIA 2014

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KEYWORDS

Flood disaster, contaminated sites, industrial sites, mine tailing

ABSTRACT

During the May 2014, exceptionally heavy rains fell on Serbia and led to a rapid increase of water levels in the main rivers in western, south-western, central and eastern Serbia. The main environmental problems include: contamination of water and land from legacy mining operations, activation of landslides and negative impacts on surface and groundwater from poorly stored hazardous chemical waste. The incident at the Stolice mine tailing in Kostajnik (Krupanj) is one of the main stand-alone environmental problems emanating from this disaster. The tailing site which holds around 1.2 million tonnes of mining waste was closed in 1987. Extremely heavy rainfall triggered a landslide which damaged the tailing drainage collection system. This resulted in excessive amounts of water accumulating within the tailing thereby undermining the physical stability of the tailing dam, which ultimately collapsed. Over 100,000 m^3 of tailing slurry was consequently released into the Kostajnik stream, a seasonal tributary of the Jadar River. Soil analysis showed the sediments to contain extremely high levels of arsenic, antimony, barium, zinc and lead requiring urgent remedial intervention. Chemicals and hazardous substances stored in industrial facilities were also impacted by the heavy rainfall and flooding. Contaminated sites of concern include the Prva Iskra chemical plant at Baric which holds around 460 tonnes of hazardous chemical waste and chemical Industry "Zorka" Sabac.

INTRODUCTION

During the third week of May 2014, exceptionally heavy rains fell on Serbia which were caused by a low-pressure system (‘Yvette’) that formed over the Adriatic. Record-breaking amounts of rainfall were recorded more than 200 mm of rain fell in western Serbia in a week’s time, which is the equivalent of 3 months of rain under normal conditions. The heavy rainfalls led to a rapid and substantial increase of water levels in the main rivers in western, south-western, central and eastern Serbia: Sava, Tamnava, Kolubara, Jadar, Zapadna Morava, Velika Morava, Mlava and Pek. In the Sava River basins where most of the rainfall was received, the consequences were two-fold. In the first place, flash floods occurred in the tributaries where water levels rose almost immediately after the onset of the rains and then dropped quickly back to normal levels when the rains stopped. The second consequence was that the level of the river Sava itself rose at a more gradual rate, with an increase of 3.5 meters recorded over the period 14-20 May. In contrast to its tributaries, the water level on the Sava peaked after the rains had stopped and decreased much more slowly after the peak (by some 20-30 centimetres per day).

The heavy rainfall and rising water levels had three immediate and direct effects:

- High intensity flash floods resulting in the total destruction of houses, bridges and sections of roads;
- Rising water levels resulting in the widespread flooding of both urban areas and rural areas; and,
- Increased flow of underground waters leading to widespread landslides.

Overall the floods affected some 1.6 million people living in 38 municipalities/cities mostly located in central and western Serbia. In addition to the negative direct effects of the floods over the population, the disaster brought about additional problems related to environmental conditions.Floods waters and rising groundwater levels covered some industrial zones and threatened to release hazardous waste with potential negative impact on health conditions of the population. Mine disposal sites were also flooded and the waste material was discharged into rivers that were used as sources for drinking water supply. Fortunately, these threats to health did not materialise as indicated by chemical analyses of the water sources.

CONTAMINATED SITES AND DAMAGES ASSESSMENT

The floods affected areas of south-western, western and central Serbia possesses diverse and important natural resources and environmental assets that are intricately linked to the economy and livelihoods of the population. These include large areas of arable land, forest resources, mountain springs and wildlife. The region is drained by important river systems including the Danube, Sava, Drina, Kolubara and Morava. Industrial activity, particularly in Sabac and Loznica, has had detrimental environmental effects. Some of the main environmental and public health risks stem from abandoned industrial facilities such as poorly stored hazardous waste at Prva Iskra in Baric. Both legacy and active mining sites such as the Stolice mine tailings and the Zajaca mining and battery recycling waste dump are also important sources of contamination risk. Results of metals concentration in soil samples near the contaminated sites are given in Table 1 and 2. Prior to the floods of May 2014, debris from demolition works in Serbia was disposed of at the nearest disposal site where it was either mixed with the normal solid waste or used, in some instances, as cover material for landfill operations.

The main environmental problems emanating from the floods of May 2014 include: (i) contamination of water and land from legacy mining operations; (ii) negative impacts on surface and groundwater from poorly stored hazardous chemical waste; (iii) activation of at least 775 landslides in the 24 priority municipalities; (iv) generation of 500,000 tonnes of debris waste requiring disposal; (iv) deforestation, forest degradation and biodiversity losses; and (vi) damages to environmental monitoring equipment.

Structural damages to infrastructure and physical assets has created an important environmental burden in two main ways: (i) damages to industrial facilities and mining operations has released hazardous substances and waste into the environment, polluting surface and groundwater as well as land with secondary impacts on ecosystems and wildlife (e.g. fish kills); and (ii) damages to houses and buildings has generated in excess of 500,000 tonnes of debris, of which 80 % is from the strip out (i.e. household furnishings and electrical equipment) of floods affected buildings and the remaining 20 % is from demolition works (concrete, brick, roof tiles, plaster, etc.). It should also be noted that some of this debris may have been mixed with hazardous substances in the buildings (batteries, solvent, oils, asbestos, etc) which can lead to environmental degradation if disposed in an unsafe manner.

The floods affected area contains both historic and active mining operations, which were impacted by the heavy rainfall and floods. The incident at the Stolice mine tailing in Kostajnik (Krupanj) is one of the main stand-alone environmental problems emanating from this disaster. The tailing site which holds around 1.2 million tonnes of mining waste was closed in 1987 and reportedly fully stabilised prior to the flood. Extremely heavy rainfall triggered a landslide which damaged the tailing drainage collection system. This resulted in excessive amounts of water accumulating within the tailing thereby undermining the physical stability of the tailing dam, which ultimately collapsed. Over 100,000 m^3 of tailing slurry was consequently released into the Kostajnik stream, a seasonal tributary of the Jadar River. Downstream of the mine tailing, the flash floods covered a land area of between 50-75 meters wide with a sediment deposit ranging generally between 5-10 cm but in some cases up to 70 cm thick. Soil analysis showed the sediments to contain extremely high levels of arsenic, antimony, barium, zinc and lead requiring urgent remedial intervention. In another instance, the pumping of an estimated 200 million m^3 of water from the flooded Tamnava-Zapadno polje open pit coal mine is also likely to increase pollution loads and effect the aquatic environment of the Kolubara River.

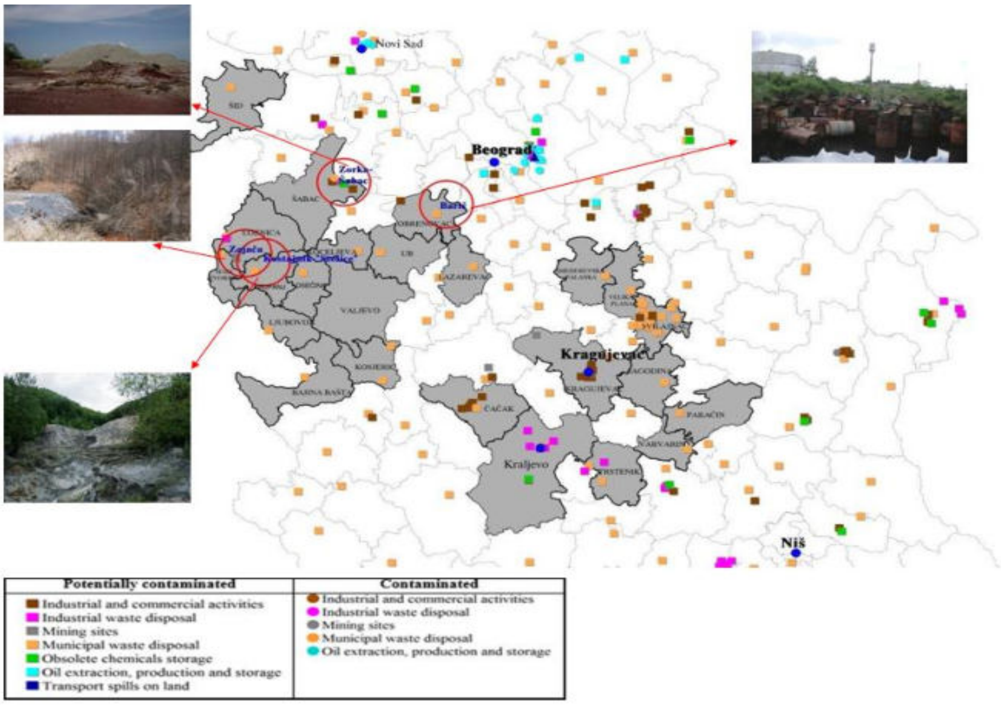

Fig. 1. Flood affected areas and contaminated sites

Chemicals and hazardous substances stored in industrial facilities were also impacted by the heavy rainfall and flooding. Notable sites of concern include the chemical industy Prva Iskra chemical plant at Baric which holds around 460 tonnes of hazardous chemical waste. A significant proportion of this waste is stored in poor and leaking containers that are only partially protected from rainfall. Although the site was not impacted by the river floods wave, contamination is likely to have occurred from rainfall overspill and rising groundwater that may have come into contact with the chemicals. This contaminated water will either drain into the nearby Sava River or infiltrate into the groundwater.

Tab. 1. Range and mean concentrations of metals in soil samples near industrial and mining sites

Metal (mg/kg)	Chemical Industry "Prva Iskra" Baric		Chemical Industry "Zorka" Sabac	
	Range	Mean	Range	Mean
Lead	<5-10.4	8.3	1065-1096.3	1082.4
Copper	13.7-35.2	27.6	1492.6-1516.4	1503
Nickel	91.5-108.7	98.7	90.8-110.7	98.3
Zinc	75.6-199.4	115.3	318.3-347.9	332.07
Manganese	482-818	594.2	726-1231	895.3
Iron	17.7-35.5	28.3	161.4-179.6	172.1

Tab. 2. Range and mean concentrations of metals in soil samples near industrial and mining sites

Metal (mg/kg)	Old tailing "Stolice" Kostajnik		Ex antimony mine "Zajaca"	
	Range	Mean	Range	Mean
Arsenic	4118.9.-4560	4272.2	327-410	376
Cadmium	9.5-13.4	11.8	0.18-0.4	0.3
Chromium	6.1-10.1	8.57	155.08-169.8	162.8
Lead	385-448	407.3	108.5-405	212.03
Copper	23.3-24.6	24.03	20.3-22.8	21.9
Nickel	14.3-17.5	16.03	32.1-39.6	36.1
Zinc	1221.4-1630	1477.4	72.7-104.7	90.8
Mercury	6.3-10	8.23		

For debris, there were no significant effects on the infrastructure to handle and dispose of the debris arising from the floods, except that the large quantities of debris contributed considerably to filling up the currently available solid waste disposal facilities. Future capacity to receive debris for disposal has therefore been seriously compromised and will require ‘reconstruction’ in the form of re-establishment of solid waste and debris disposal sites.

Environmental inspectors visited the total of 25 public municipal landfills and based on inspection they confirmed that five landfills were under the influence of flood in (Obrenovac, Koceljeva, Ub, Vrnjačka Banja ans Varvarin) from which the material was completely or partially taken away on surrounding roads, arable land or into torrential water. Only the landfill in Vladimirci was partially exposed to underground water, and a small amount of waste was scattered around the surrounding agricultural land.

The considerable amount of debris generated by the floods is significant compared to normal daily and monthly generation levels. As a result, local solid waste management systems have been put under considerable strain to deal with the large debris quantities.

There are two main negative environmental impacts from the large quantities of debris arising from the floods clearance works: (i) large quantities of debris have contributed to the ‘filling’ up of existing solid waste disposal facilities and has therefore exacerbated the requirement for additional debris and solid waste disposal facilities in the floods affected areas; and (ii) debris is typically not sorted (especially that from strip out works in the first months following the return of residents to their homes) and thus is likely to contain hazardous wastes, which when disposed of in an uncontrolled landfill, can lead to environmental damages to groundwater and water courses.

Agricultural lands were also tested for potential contamination by the Ministry of Agriculture and Environmental Protection in order to ensure that vegetables and food crops would not be contaminated with heavy metals. While generally heavy metal contamination was not found to be a problem, in some localities (e.g. Cacak, Kraljevo, Smederevska Palanka, Jagodina) concentrations of nickel, lead and chromium, were found at certain sites to be above the maximum permitted level. Other sites such as in Kosjerić and Loznica were found to have high levels of lead and arsenic. Restrictions were therefore imposed on the types of crops that could be grown, and special measures such as ploughing are required to reduce contamination levels. Although these are generally short-term measures that are unlikely to extend beyond the growing season, it nevertheless implies a loss of revenue and additional labour by farmers.

EFFECT ON RISK AND VULNERABILITIES

While no acute human exposure from toxic chemicals and hazardous waste releases were recorded from the floods, several contaminated ‘hot spots’ pose serious risks of localised chronic exposure in the medium to long-term. The collapse of the Stolice tailing dam and the impoundment created by water overflow into the Zajaca mining and battery recycling waste dump are two important cases in point. For example, analysis of Stira stream waters directly downstream from the Zajaca waste piles revealed it to contain extremely high levels of arsenic and antimony. Given their vulnerability to pollution, groundwater and surface water as well as aquatic life and fish will require regular monitoring particularly around suspected contaminated sites.

LEGAL FRAMEWORK FOR ENVIRONMENTAL LIABILITY

In the Republic of Serbia, several regulations regulate the contaminated sites management and environmental liability. The Law on environmental protection (“Official Gazette of the Republic of Serbia”, No. 135/2004, 36/2009, 36/2009 – other Law, 72/2009 – other Law and 43/2011 – decision of Constitutional Court) is the basic law which establishes the system of environment protection in the Republic of Serbia. This Law defined that rehabilitation, i.e., remediation is the process of undertaking measures in order to halt pollution and further degradation of environment up to the safe level for future use of the location, including also the arrangement of the area, revitalization and recultivation thereof. The Low describes the “polluter pays” principle.

According to Article 16 of this Law, any person who degrades the environment is obliged to perform recultivation or to rehabilitate in any possible way the degraded environment in accordance with this and special laws. According to Article 43 of this Law, the status of endangered environment and the regime for rehabilitation and remediation in an area of importance for the Republic shall be determined by the Ministry which is responsible for the environment, and for an area of local relevance by the local self-governance unit.

There is no specific regulation regarding the environmental liability in the Republic of Serbia, but some provisions of the Directive 2004/35/CE are comprised within the Law on environmental protection of 2004 and the Regulation on the program for systematic monitoring of the soil quality, indicators for evaluation of soil degradation and methodology for preparation of remediation program of 2010.

In Serbia, the question of contaminated site’s liability is dealt according with the principle of polluters and legal successor’s liability. This means that any legal or natural entity who shall be involved in environmental pollution by its illegal or improper activities shall be liable in compliance with the law. The polluter or its legal successor shall be bound to eliminate the cause of pollution and the consequences of direct or indirect environmental pollution and, in addition to that, the polluter shall be liable for environmental pollution also in the case of liquidation or bankruptcy of the company or other legal entities, in accordance with the law.

Furthermore, when changes in the ownership of companies or other legal entities or other changes in the ownership structure occurs, an assessment and allocation of liability for environmental pollution, and settlement of debts (charges) of the ex-owner on account of pollution or damage to the environment shall also happen. It is also possible that the liability to be passed, contractually, from the polluter to a purchaser of the contaminated site.

However, when the polluter is unknown, the principle of subsidiary liability is applicable. This means that state authorities, within their financial abilities, shall eliminate the consequences of environmental pollution and reduce damages when the polluter is unknown, and when pollution originates from the sources outside the territory of the country. When contamination is new, it can be managed in a regime of emergency.

The vision for ensuring an environmentally sound flood recovery and reconstruction plan is based on a building back approach to help resolve important long-standing environmental challenges.

It is informed by the objectives of Serbia’s National Environmental Protection Programme and Spatial Plan that are both valid until at least 2020, and which are aligned with European Union programmes and standards. Guiding principles include:

- Reduce and prevent pollution from contaminated sites and mine tailings impacted by floods and heavy rains to protect public health and the environment;
- Within the framework of the national Spatial Plan, review, develop and enforce disaster sensitive land use plans as the most effective investment to protect people and property from extreme flood events;
- Ensure that debris is handled and disposed of safely whilst seeking opportunities to reuse and recycle debris materials where possible and practicable;
- Promote an ecosystem management approach to disaster risk reduction including rehabilitation of flood plains to create ”space” for water to overflow and forestry measures that help improve soil stability and reduce risks where possible;
- Strengthen the application of a river basin management approach to increase the effectiveness of flood prevention and protection measures.

CONCLUSION

A two-phase, Environmental Recovery and Reconstruction Plan for contaminated sites, is proposed consisting of:

1. Short to medium term measures of up to two years
    - Reconstruction of the Stolice mine tailing dam and site rehabilitation.
    - Priority contaminated sites should be assessed and immediate safety measures implemented. Priority sites include the mining and battery waste dump at Zajaca and poorly stored hazardous waste at the Prva Iskra Baric chemical plant. Where necessary, hazardous waste stocks should be exported for safe disposal in accordance with the provisions of the Basel Convention on Hazardous Waste.
    - 100% of the debris from the streets of flood affected areas is removed and disposed of at designated disposal sites in an environmentally safe manner.
2. Long term measures
    - Within the framework of the Spatial Plan, re-evaluate land use plans to ensure that they are disaster sensitive. These plans should take into account as minimum flood returns of 100 years but also extreme floods of 1,000 years, based upon solid analysis of past events and climate change scenarios including hydrological modelling for both the large river basins and smaller catchments susceptible to flash floods. In this context, it is critical that all hazardous waste is removed from flood prone areas to safer grounds, including those in the industrial facilities at Sabac.
    - To ensure effective implementation of land use plans, revision and harmonization of relevant legislation should be conducted including of the Law on Planning and Construction (Official Gazette 98/13), Law on Emergency Situations (Official Gazette 93/12), and Law on Mining and Geological Research (Official Gazette 88/11).
    - Comprehensively assess the underlying environmental risks associated with the Stolice tailing mine and the Zajaca waste dump that have been exposed by the floods. This may require a decommissioning of these high risk sites. Options may include recovery of valuables from the tailings using modern separation technology. If this is not economically feasible and the environmental risks are deemed unacceptable, international best practice is to relocate the waste into a new purpose built hazardous waste landfill. Groundwater pollution should be monitored and remediated, if found. Both sites should be re-landscaped and land use restrictions placed on them. Assuming that groundwater pollution will not require long term and complex remediation, the entire restoration project could cost approximately 50 million US dollars.
    - Strengthen the capacity for environmental monitoring and reporting to improve environmental management and performance. This will help improve the supervision of contaminated sites, assess the effectiveness of remedial measures and limit potential exposure to pollution.

Generally, Serbia has limited data on the impact of past disaster events. There is a need for generating more information on risk. While a number of geographic and hazard specific assessments have been conducted, there has been no comprehensive national level risk assessment. In addition, these assessments have only focused on flooding of larger and smaller rivers, excluding the risk of flooding caused by torrents. Effective floods risk management will require a better understanding of the causes of different types of flooding, their probabilities of occurrence, and their expression in terms of extent, duration, depth, and velocity. In this context, it will also be essential to understand how floods risk will evolve over time given the changing climate.

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MODIFIED FENTON'S REAGENT: EXPLOSIVE ZONE (EX-1) APPLICATION CONTROL AND SAFETY MANAGEMENT

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KEYWORDS
In situ chemical oxidation, Modified Fenton's reagent, explosive zone (EX-1), real time monitoring, BTEX, aerobic transformation.

SUMMARY

Contrary to previous decades, the complexity of remediation projects in the Central Europe rapidly increases as the sites became gradually more *difficult-to-treat* (be it for the complexity of geological and hydrogeological background, or due to complicated surface conditions). Moreover, the recent development of environmental applications driven by the political emphasis on low cost and time effectiveness forces the project managers to choose quicker and more definite solutions to ecological problems. This paper describes the pilot deployment of *in situ* chemical oxidation (ISCO) using the Modified Fenton's Reagent (MFR) for the remediation of a heavily BTEX-polluted site located within the grounds of active petrochemical plant. Aside from site specific functionality verification, the study tested possible ways of *real time* reaction control and project safety management in the immediate vicinity of explosive zone (EX-1). The monitored risk-factors included the exothermic character of the reaction, the corrosiveness of injected reagent, the groundwater level (with regard to the depth of local industrial utility networks), and the generation of volatile organic compounds (VOCs) as pollutant oxidation daughter products. The effect of ISCO application on ambient microbial communities was also evaluated. Aside from successful decontamination of the target zone, we provide an insight on the interaction between injected MFR and selected environmental parameters. Using standard as well as advanced monitoring tools for the application control and safety management, we present a year-long data series depicting the transition of physicochemical parameters from pre-treatment (anaerobic), through treatment (aerobic), to post-treatment (anaerobic) conditions.

INTRODUCTION

Recent political development emphasizes the cost and time effectiveness of all environmental applications proposed in the Central Europe. Conventional physical treatment-based methods, such as pump-and-treat, air-sparging, or venting, are usually ineffective when a complete remediation in time and budget-limited projects is needed. This is even more evident when dealing with complex conditions (e.g., geological and hydrogeological settings or continuous on site industrial activity, etc.) of the target site. In contrast to 1990s and early 2000s, when the majority of less challenging sites was addressed, the focus of remediation projects has shifted towards more *difficult-to-treat* sites in the past decade. Quicker and often more intense technologies are being deployed in order to remediate human impacted environments and to get the level of contamination below the specified concentration limits. These innovative methods commonly requiring *in situ* application are often based largely on the chemical or physicochemical processes.

One of the major advantages of *in situ* treatment technologies is the remediation cost and time reduction by avoiding the excavation and processing of the contaminated soil/rock. Another significant time-saving can come from the use of the technology itself as it has – when applied properly – the potential for considerable contaminant destruction within weeks or months from application. Further, *in situ* techniques provide a tool suitable for the remediation of a wide range of contaminants from light non-aqueous phase liquids (LNAPLs), through dense non-aqueous phase liquids (DNAPLs), to persistent organic pollutants (POPs), and polychlorinated biphenyls (PCBs), with a broad interval of pollutant concentrations treatable[1].

In situ chemical oxidation (ISCO) is an important member of the above mentioned innovative technologies. This approach is based on the infiltration of aqueous solution of an oxidizing agent into the ground, which leads to the destruction of pollutant either dissolved in the groundwater, sorbed on the soil matrix, or present as a free phase product[2]. In general, ISCO is usable for the remediation of unsaturated as well as saturated zone for any type of pollutant that can be oxidized to nontoxic or less toxic daughter products[3]. However, most often the method is referenced for the remediation of saturated zone polluted with chlorinated ethylenes[4], hydrocarbons of the BTEX[4] group (benzene, toluene, ethylene, and xylenes), polycyclic aromatic hydrocarbons[4] (PAHs), PCBs[4], chlorobenzenes[5], and others.

Fenton's Reagent (FR; the mixture of H_2O_2 and Fe^{II}) is a frequently used ISCO oxidant for the remediation of petroleum hydrocarbon-contaminated sites[5, 6]. The Fenton's reaction generates hydroxyl radicals $OH^{\bullet}$ (eq. 1) and other reactive oxygen species (ROS), and the oxidation end products include CO_2, water, and iron oxy-hydroxides. Due to its high reactivity and low cost, H_2O_2 is preferred by many project managers as the best oxidant of choice. However, several crucial considerations must be kept in mind during the use of FR for the remediation of polluted environment. The FR is highly instable oxidant with exothermic decomposition that releases high amounts of O_2. Moreover, in reaction with organic contaminants, FR can produce high amounts of volatile organic daughter products (VOCs) posing a significant threat to the operation health and safety protocol. The nonspecific loses of the oxidant during *in situ* application (such as non-radical decomposition of H_2O_2 by the reaction with ambient Fe or Mn) present another vital factor potentially decreasing the overall reaction strength[3]. Thus, stabilization and optimization of the reaction conditions is a vital factor when it comes to FR-deploying ISCO. Various modifications have been devised for the FR with the main objective in keeping the reacting iron in dissolved state[7]. This is often achieved by lowering the solution pH, despite it makes the reagent more corrosive to subsurface constructions (e.g., building foundations or utility networks) potentially present at the site. Therefore, the main limitations for using FR remain in the work safety management and the control of the reaction plume within the contaminated target zone.

$$H_2O_2 + Fe^{2+} \rightarrow HO^{\bullet} + HO^{-} + Fe^{3+} \qquad (E^{\circ} = 2{,}59\ V)^{3} \qquad (1)$$

This presentation describes the pilot application of modified Fenton's Reagent (MFR – with the addition of citric acid) for the intensification of conventional methods used to remediate petroleum hydrocarbon contaminated environment. Pollutants of concern were benzene, naphthalene, and other non-polar organic compounds (NOCs). The target site is located within the actively producing grounds of petrochemical plant Unipetrol RPA, ltd. (Litvinov, Czech Republic) and it covers the area of 530 m^2. The target unconfined anthropogenic sandy-gravel aquifer is about 3 m thick with estimated porosity of 0.15 and it is underlaid by an isolating layer of tertiary clays. The contaminated groundwater table reaches 1.5 m bgs (below ground surface). The groundwater flows generally in the NE–SW direction with the average hydraulic conductivity $K = 2.6 \times 10^{-4}\ ms^{-1}$.

The chief objectives of this test were 1) to verify the functionality and usability of the technology in the target site conditions, 2) to reduce the pollutant content to set levels, 3) to avoid compromising the rigorous safety regulations within the immediately adjacent explosion zone 1 (EX-1), 4) to define and optimize on site techniques for simultaneous monitoring, evaluation, and control of oxidation processes (on site *real time* monitoring), and 5) to evaluate the effect on the ambient microbial communities. The risk-factors of interest included 1) the exothermic course of oxidation (a requirement to keep the maximum groundwater temperature below 25 °C), 2) the corrosiveness of the groundwater (due to the MFR stabilization with citric acid – a requirement to maintain the groundwater pH $\geq$ 4,5 (corrosiveness limit) and the groundwater table below the level of local utility networks), and 3) VOC generation (ISCO daughter products – a requirement for venting and monitoring of the VOC concentrations in the target zone).

METHODS

Project design. The total of seven application events was carried out between Nov-13-2013 and Jan-28-2014 in order to inject 77 m^3 of 5 % (w/v) MFR. The complete situation of the pilot-testing field including injection, venting, and monitoring well networks is shown in Figure 1. To simulate dynamic flow conditions (expected during the full scale remediation) at the pilot testing field, the groundwater was pumped from the well HV-8857 in between particular injection events. The pumped water was cleaned on high-pressure sorption filter (WAF 1200 DT) with granular activated carbon and recycled back into the remediated zone to increase local hydraulic gradient and to enhance remediation of the capillary fringe by flushing. Due to the generation of significant amounts of VOCs as oxidation daughter products, *in situ* soil venting was used to extract and clean the gases with activated carbon filter.

Field monitoring. Every MFR application event was monitored on site for the *real time* changes in groundwater level and temperature using automatic sensors Levelogger (Solinst, George Town, Ontario, CAN) and for the decrease of H_2O_2 concentration using the field photometer MD 600 (Lovibond, Dortmund, GER). Along with the applications, field monitoring of the groundwater physicochemical parameters (red-ox (ORP), dissolved oxygen (DO), electric conductivity (EC) and pH were regularly performed using Lovibond MicroDirect electrodes and the pocket oxygen meter MKT 44A (INSA, Praha, CZE). Concentrations of VOCs in the soil air were regularly monitored using the photoionization detector (PID) MiniRAE3000 PGM-7320 (RAE Systems, San Jose, CA, USA).

Laboratory analyses. The development of microbial communities in response to changes in environmental conditions was evaluated by cultivation as well as epifluorescence (Nicon Eclipse 50) methods. The pollutant concentrations were regularly analyzed in an accredited laboratory.

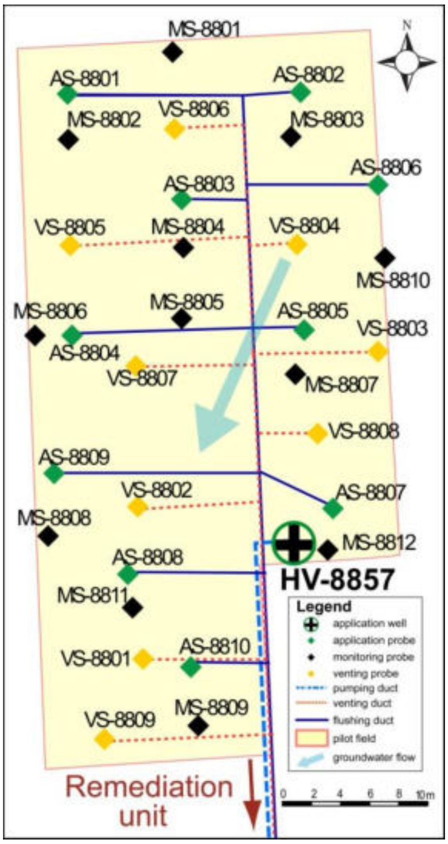

Fig. 1. Pilot field situation.

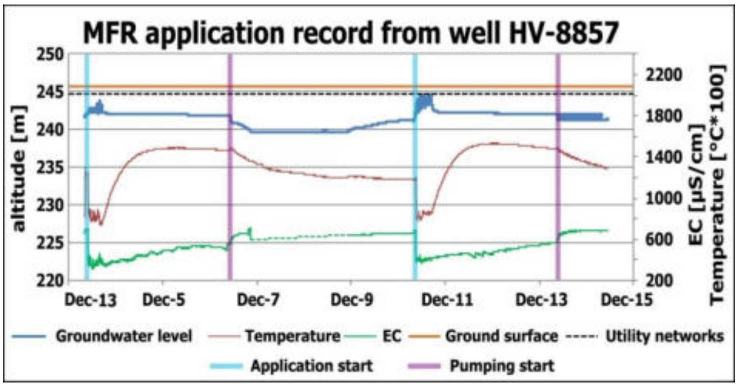

Fig. 2. Example of the *real time* monitoring of groundwater level, temperature, and EC (electric conductivity) between two application events.

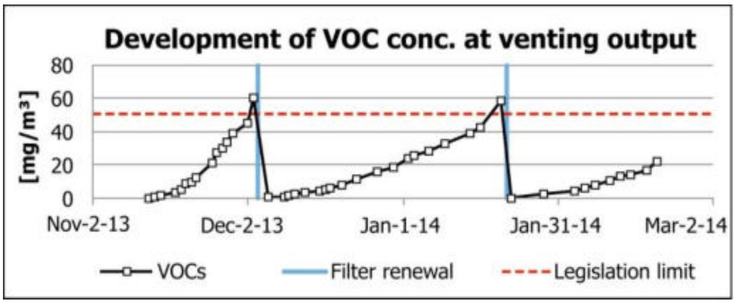

Fig. 3. Venting system efficiency during the pilot test.

RESULTS AND DISCUSSION

***Real time* monitoring.** An example of the automatic groundwater level, temperature, and EC logging performed in the application well simultaneously with the oxidant injection is shown in Figure 2. The application start had an obvious effect on the immediate development of all three parameters studied: groundwater level rise, temperature drop (due to the preparation of reagent solution in cold winter conditions), and EC drop (due to low mineralization of the MFR). After the initial peak in groundwater level, caused by the rise of the water column in the well, the parameter stabilized showing that even inside the well casing the groundwater table did not exceed the depth of the utility networks. Considering the conical shape of the groundwater table around the application well and the relatively high hydraulic conductivity (see the introduction part), the requirement to keep the groundwater table below the level of local utility networks was undoubtedly fulfilled.

The expression of the oxidation exothermic character was observed after reagent injection. However, the 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 3 shows the development of VOC concentrations on the output of the venting filter (Activated carbon – AC). The three rising VOC concentration curve segments show lessening slope steepness, which indicates increasing AC filter durability as the reaction intensity gradually decreased over time (with decreasing pollutant concentrations). Moreover, field monitoring of the target zone VOC levels (directly from monitoring probes) provided additional proxy data on the situation of residual contaminant present in the aquifer and thus aided as an application targeting tool.

Physicochemical parameters. Long-term monitoring of pH, ORP, and DO displayed the response of environmental conditions to the oxidant application (Fig. 4, 5, and 6, respectively). The development of pH values (Fig. 4) exhibited rapid changes mainly in the application well HV-8857. The second most evident were the pH changes in the central-field monitoring probe MS-8805 and least pronounced was the response of pH in the monitoring probe MS-8801 on the inflow edge of the test field (Fig. 4). Despite the sharp declines in the application well HV-8857, the 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 measures addressing the groundwater corrosiveness (groundwater level and pH) were successfully observed.

The development of ORP (Fig. 5) presented the efficiency of the ISCO technology. Not only in the application well, but also in the monitoring probes, the groundwater red-ox conditions responded promptly to the MFR application reaching values up to 400 mV. Along with the ongoing oxidation, the elevated ORP tended to drop back after each application and exhibited gradually higher return-values as the number of application events rose. This was interpreted as progressing degradation of the pollutants and other ambient organic compounds present in the target zone. Conversely, lower ORP return-values indicated areas with persistent presence of the pollutant. Thus, together with the field VOC level monitoring, the measurements of ORP helped focusing the MFR application in the latter part of the pilot study.

According to expectation, the DO concentrations increased throughout the test field upon the MFR injections (Fig. 6), with the application well HV-8857 regularly exhibiting DO values above the instrument detection limit (20 mg/l). The development of DO parameter indicated direct transformation of environmental conditions from anaerobic (before the study) to aerobic (during MFR applications) and back to anaerobic (after pilot test termination). These rapid changes likely forced the ambient microbial communities to appropriate shifts in metabolic preferences, benefiting mainly species capable of facultative metabolism.

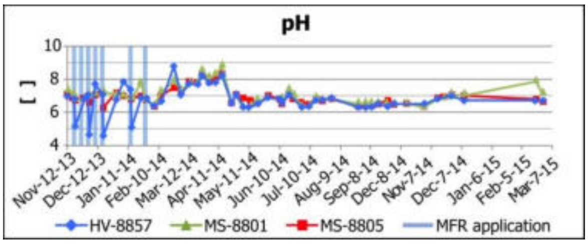

Fig. 4. Development of pH after MFR application.

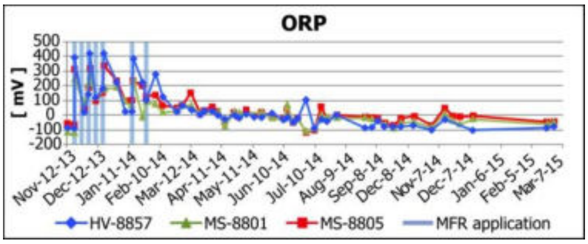

Fig. 5. Development of ORP after MFR application.

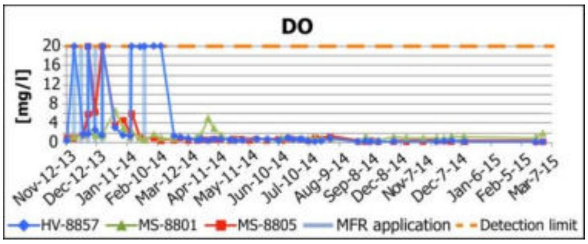

Fig. 6. Development of DO after MFR application.

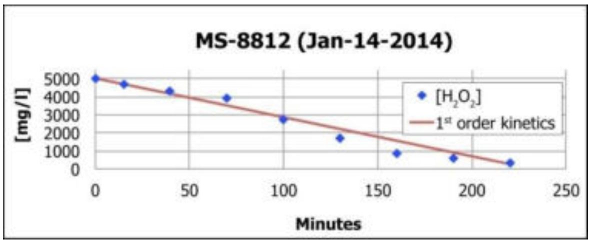

Fig. 7. Hydrogen peroxide utilization kinetics example from targeted MFR application.

Hydrogen peroxide utilization. Figure 7 shows an example of H_2O_2 degradation kinetics on site monitoring performed during one of the targeted MFR application (based on the measured VOC and ORP values evaluation). The field measurements followed after the MFR injection and revealed the 1st order-like (quasilinear) kinetics of the oxidant degradation in the environment. Field measurements of oxidant concentrations further aided with MFR application targeting: the quicker the oxidant degradation, the higher probability for remnant pollutant presence in the monitored area. With time, the H_2O_2 degradation slowed down across the test field indicating the decrease in oxidable matter content. Consequently, the MFR oxidation zone range increased with the active reagent being carried further from the injection point by groundwater flow.

Pollutant concentration monitoring. Table 1 contains thepollutant concentration history as recorded in the well HV-8857. The values display the positive effect of the applied ISCO technology. To obtain a 2D representation of the contaminant level response across the entire test field, generalized contour maps were constructed using the Surfer mapping software (Golden, Colorado, USA). Figure 8 shows the comparison of pollutant concentrations before and after the pilot study. The concentration gradient slopes revealed by the post-application monitoring generally respect the direction of local groundwater flow.

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

CONTAMINANT	Benzene [µg/l]	Naphthalene [µg/l]	NOC [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

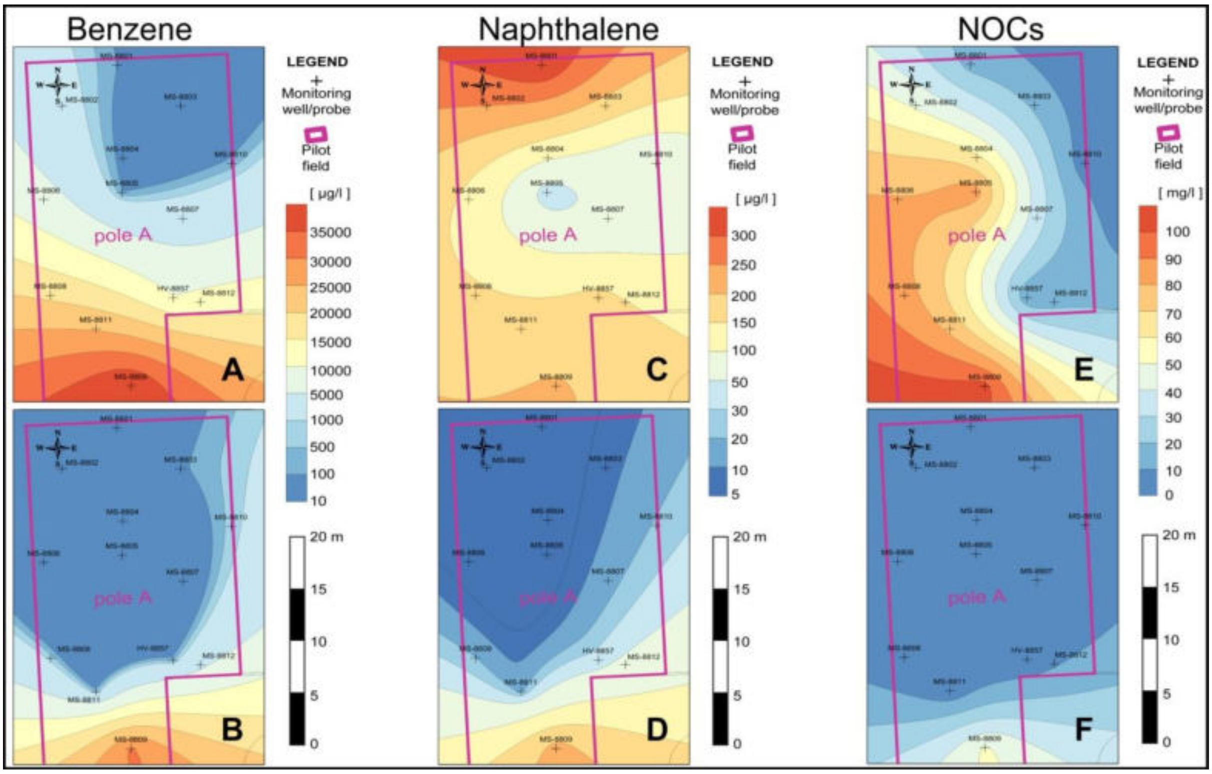

Fig. 8. Pollutant concentrations: before the pilot study – A, C, E (Nov-2013); after the pilot study – B, D, F (Feb-2014).

Water and air pumping. During the pilot test a total of 550 m^3 of contaminated groundwater and a total of 163,392 m^3 of contaminated air were pumped from the ground and the overall amounts of contaminants removed were approximately 4.0 kg benzene, 0.075 kg naphthalene, and 10.0 kg NOC in the groundwater and over 130 kg of VOCs in the pumped air. It is noteworthy that the relatively high VOC yield was achieved mainly due to the agitation of pollutants by the oxidation reaction.

Enhanced natural attenuation: Monitoring of ambient microbial (aerobic and anaerobic, heterotrophic and pollutant-degrading) populations was performed along the pilot study (data not shown). Both the cultivation as well as epifluorescence microscopy methods indicated that the ISCO technology did not cause complete destruction of the present communities. Nutrient-rich solutions were injected following the pilot study in order to support the natural attenuation processes, to prevent the contamination rebound effect, and to assist faster recovery of the ambient microbial ecosystem.

CONCLUSION

The pilot study outcome can be summarized by the recapitulation of defined objectives: 1) the effectiveness and feasibility of the remediation using MFR in the target site conditions was confirmed, 2) contamination levels were reduced by several orders of magnitude within the two months of application, 3) safety requirements of the explosive zone (EX-1) were fulfilled without reservation, 4) tools for the *real time* monitoring and process control were tested and optimized for future full-scale application, and 5) the ISCO application did not have a detrimental influence on the ambient microbial communities.

The study of risk-factors revealed the following findings: 1) the groundwater temperature increased less than 5 °C due to the exothermic oxidation character, 2) for the entire course of the pilot study the groundwater table remained below the level of local utility networks and the groundwater pH maintained values above the corrosiveness limit (pH = 4.5), and 3) the amounts of generated VOCs (ISCO daughter products) decreased over time as the intensity of oxidation reactions diminished.

Despite the strenuous site conditions in the vicinity of explosive zone (EX-1), the ISCO technology using Modified Fenton's regent is fully feasible for the projected remediation. Compared with conventional remediation methods, the use of *in situ* chemical oxidation technique provides considerable cost and time savings. The pilot study was concluded with the injection of nutrient-rich solutions to support the renewal of natural attenuation processes.

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COMPARISON OF IN-SITU TECHNICS FOR SOIL REMEDIATION

Florie Jousse

INTRODUCTION

Pollution of soils and aquifers by Diesel fuel compounds is a widespread remediation issue. Problems due to soil remediation are more and more difficult to treat. Soil is a sensitive and complex system. A lot of soil remediation technics are developed, but none comparisons have been made. So, the purpose of this study is to expose to different processes of remediation in a similar porous media system. Efficiency comparison of oxidants is realized on batches contaminated by Diesel fuel, benzene, toluene and xylene (BTX) compounds in two different matrixes, with or without organic matter. In the second step of the study, some technics are compared on column. Technics compared are, *in-situ* chemical oxidation by activated persulfate, Fenton's reagent and ozone, thermal treatment, sparging and flushing by surfactant.

MATERIALS AND METHOD

Comparison of oxidants on batches

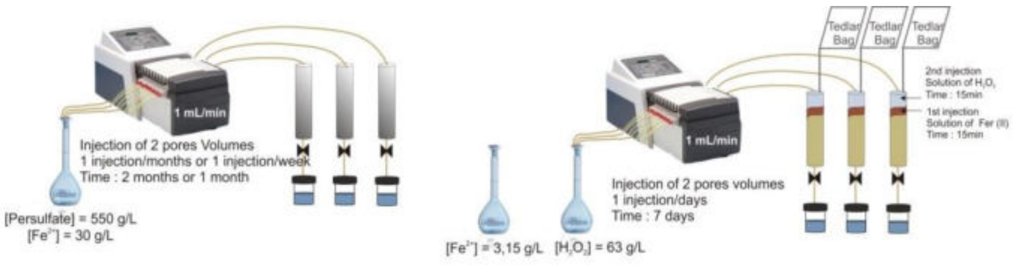
The opaque vials used in the experiments had a volume of 75 mL. Each vial was filled with 20 g of soil (fine sand or natural soil), 30 mL of demineralized water and 100 µL of Diesel fuel mixture. For each treatment, three identical vials were assembled and followed.

An excess of oxidant was added (Table 2). The batches were shaken at 300 rpm during 24h for oxidants with a rapid reaction, Fenton's reagent and Ozone. The batches for the slow oxidants permanganate and persulfate were shaken during 20 days with the same rate. A blank was realized for each experiment. A second kind of batch was realized with BTX mixture (Table 3). In 12 mL vials, 2 g of soil (fine sand or natural soil) was added with 2 mL of demineralized water. A volume of 2 µL of BTX mixture was added at 0°C to avoid volatilization of BTX.

After addition of oxidants, the batches were shaken during 24h or 20 days for permanganate and persulfate batches). Oxidant concentrations were calculated to be in large excess in relation to the stoichiometry of the oxidative reaction. The objective was to differentiate the reaction efficiency without potential limitation of oxidants. A blank was realized for each experiment.

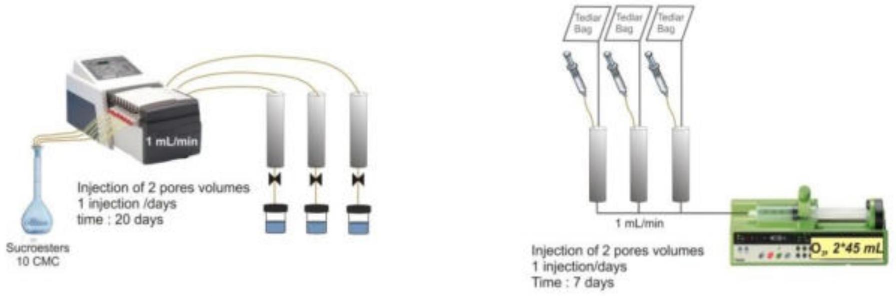
Comparison of in situ treatment on column

Stainless steel column used in the experiments had a diameter of 39 cm, effective length of 11 cm and a pore volume of 49,5 mL. Each column was filled with sand (MI 31, Sibelco, France) with a permeability of 10^{-4} m/s. The sand was polluted by a mixture of decane ($C_{10}H_{22}$, Fisher, France) and menthol ($C_{10}H_{20}O$, Fisher, France) 1:1 (v) or by a mixture of benzene (C_6H_6, Baker, France), toluene (C_7H_8, 98% Fisher, France) and o-xylene (C_8H_{10}, 98% Fisher, France) 1:1:1 (v). The saturation of the two pollutant mixture was 6%. The choice to use menthol in a first experience can be explained by the same propriety of solubility of this compound in relation to the solubility of BTX and because this compound is less toxic than BTX. Sand, water, and pollutants were mixed in a beaker to obtain a homogeneous mixture. Sand polluted was placed into column and he was packed. In these experiments, six treatments were applied and three columns were used for each experiment (Fig.1. and Table 1).



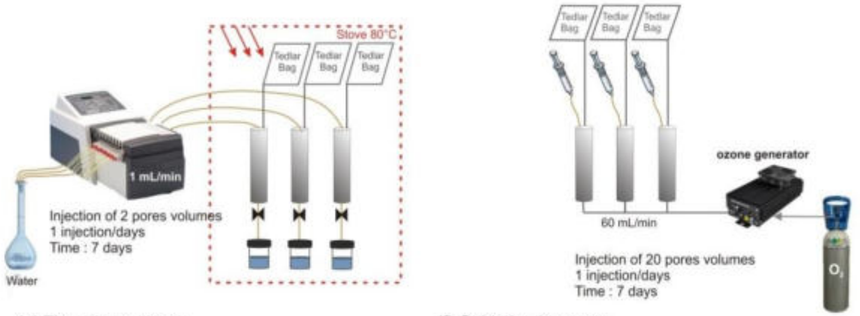
(a) Oxidation by activated persulfate

(b) Oxidation by Fenton 's reagent



(c) Flushing by surfactant (Tween 80)

(d) Sparging treatment



(e) Thermic treatment

(f) Oxidation by ozone

Fig.1.

(a) Oxidation activated persulfate with iron (II) implementation on column
(b) Oxidation with Fenton's reagent implementation on column
(c) Surfactant flushing (Tween80) on column
(d) Sparging treatment implementation on column
(e) Thermic treatment at 80°C implementation on column
(f) Oxidation by ozone implementation on column

Tab. 1. Descriptive of treatments applied on column

Treatments	**Concentration of oxidants and surfactant**	**Volume injected (pore volume)**	**Number of injection**	**Duration of experiments**
Oxidation by activated persulfate	$[Na_2S_2O_8]$ = 550 g/L $[FeSO_4^{2-}]$ = 27,8 g/L	2 PV*/day	1/month	2 months
Oxidation by Fenton reagent	$[H_2O_2]$ = 63 g/L $[FeSO_4^{2-}]$ =3,15 g/L	2 VP/day	1/day	7 days
Oxidation by Ozone	10,5 g	20 VP/day	1/day	7 days
Surfactant flushing (Tween 80)	10 CMC	2 VP/day	1/day	20 days
Sparging		2 VP/day	1/day	7 days
Thermic treatment		2 VP/day	1/day	7 days

***Pore volume**

RESULTS AND DISCUSSION

Experiences on batches

Hydrocarbon oxidation in fine sand matrix

Fig.2 shows the results of hydrocarbon oxidation by four oxidants. Permanganate oxidation during 20 days resulted in 100% of toluene and o-xylene removal but no benzene removal. Around 40% of n-undecane and n-dodecane were removed and only 20% of n-heptadecane and 10% of n-octadecane.

Oxidation during 20 days by persulfate activated with iron (II) was applied, using a molar ratio $S_2O_8^{2-}/Fe^{2+}$ of 1/0.1 [1,2]. After 20 days of reaction, 100% of BTX compounds were removed. Around 85% of n-undecane, 80% of n-dodecane, 60% of n-heptadecane and 50% of n-octadecane were removed.

Fig. 2 demonstrates a total removal of benzene, toluene and o-xylene by Fenton's reagent or ozone oxidation after 24h of reaction. Around 80 % of n-undecane, 70% of n-dodecane as well as 40% of n-heptadecane and n-octadecane were removed by Fenton's reagent oxidation. Ozone oxidation permitted to remove 95% of n-undecane and n-dodecane, 40% of n-heptadecane and n-octadecane within 24h of reaction.

For all oxidants, a decrease of degradation rate as a function of number of carbon atoms in Diesel fuel compounds was clearly observed.

Potassium permanganate is able to remove only aromatic compounds with alkyl substitution onto the aromatic ring (toluene and o-xylene), but fails to oxidize benzene. A precipitation of manganese oxides during oxidative reaction was observed during the experiments. These oxides could cause clogging of aquifers or soil pores. Permanganate is thus the poorest oxidant at Diesel sites.

Studies realized with Fenton's reagent and ozone showed a complete efficiency of both oxidants on BTX in short time (24h). Fenton's reagent treatment showed a high efficiency on more toxic aromatic fraction [3]. In natural soil, Fenton's reagent showed a better efficiency on n-alkanes than in pure sand. The presence of iron oxide in natural soil may explain this increase in removal rate. Indeed, Usman [4], showed a high degradation of n-alkanes (>80%) with Fenton's reagent in presence of magnetite. Kong [5], showed an influence of iron oxide minerals presence on Fenton's reagent efficiency. These iron oxide minerals are described like catalyzers of Fenton's reaction and they are naturally present on soil matrix. Ozone showed complete removal of BTX in sand and natural soil. These oxidants oxidize aromatic compounds and n-alkanes in the same timeframe and with similar efficiency.

The experiments showed that activated persulfate removed the totality of mobile compounds BTX in 20 days. Those results indicated that sufficient contact time is a key factor for the efficiency of persulfate oxidant [6,7]. In pure sand, persulfate showed a high removal rate of BTX and n-alkanes. But also in natural soil with organic matter, BTX were completely removed, while for n-alkanes a decrease of removal rate with n-alkanes length was shown.

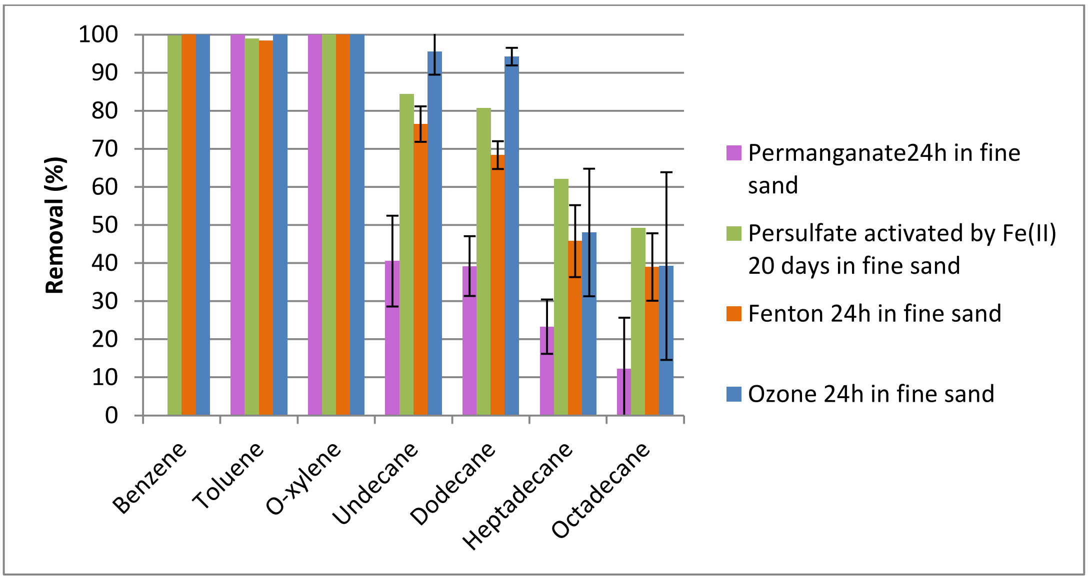


Fig. 2. Hydrocarbon removal from Diesel fuel by permanganate, Fenton and ozone after 24h and persulfate after 20 days of treatment in fine sand

Hydrocarbon oxidation in natural soil matrix

Fig. 3 shows hydrocarbon oxidation by activated persulfate and permanganate during 20 days and hydrocarbon oxidation by Fenton's reagent and ozone during 24h in a natural soil matrix containing organic matter (OM). For permanganate, natural soil matrix induced an increase of removal rate of benzene by 26%, 5.5% increase of n-undecane, 1% increase of n-dodecane, 12% increase of n-heptadecane and 23% increase of n-octadecane.

An increase of removal rates of all alkane compounds (20%, 28%, 22% and 36%) was also observed after Fenton's reagent oxidation in natural soil matrix. Hydrocarbon oxidation in ozone batches revealed no differences between fine sand and natural soil.

For activated persulfate, Fenton's reagent and ozone experiments, the total amount of BTX were removed showing no significant interaction of natural organic matter in presence of an excess of the oxidant.

In the classical approach the soil NOD is measured and a minimum dose of oxidant is calculated by adding NOD to the pollutant oxidation demand. On the other hand, supplying oxidants in excess of the stoichiometric rate is a rather typical condition of oxidant addition. When using these high concentrations in our experiments, the presence of natural organic matter did not seem to modify the efficiency. Moreover, for some oxidants the presence of organic matter seems to play the role of a catalyst, enhancing the oxidant efficiency. The previous results also showed that the oxidants first consumed BTX and then n-alkanes. One may therefore assume that natural organic matter will also be consumed after the major soluble pollutants. The classical approach of considering NOD seems therefore not be adapted in presence of hydrocarbon mixtures at high oxidant concentrations, it is more important to take under consideration the amount of alkanes. We also showed that high concentrations of oxidants are better than low ones to remove BTX and that even at these concentrations, a significant proportion of n-alkanes are oxidized.

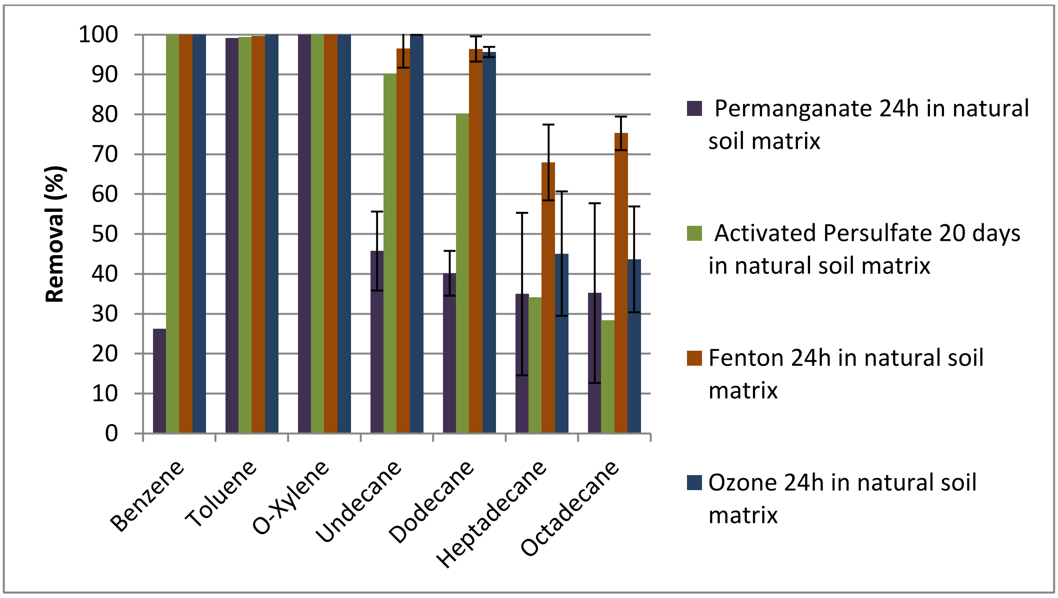


Fig.3. Hydrocarbon removal from Diesel fuel in a natural soil matrix

Experiences on column

Fig.4 shows hydrocarbon oxidation by persulfate activated by iron (II). The first experience was made on persulfate with one injection per week. The removal rate obtained was 10% and 95% for decane and menthol respectively. For the experience with one injection per month, removal rate of decane was increased to 45%. For menthol, removal was remained close to 95%. Ativated persulfate with iron (II) removed menthol equally after 1 month of treatment with one injection per week or after two months of treatment with one injection per week.

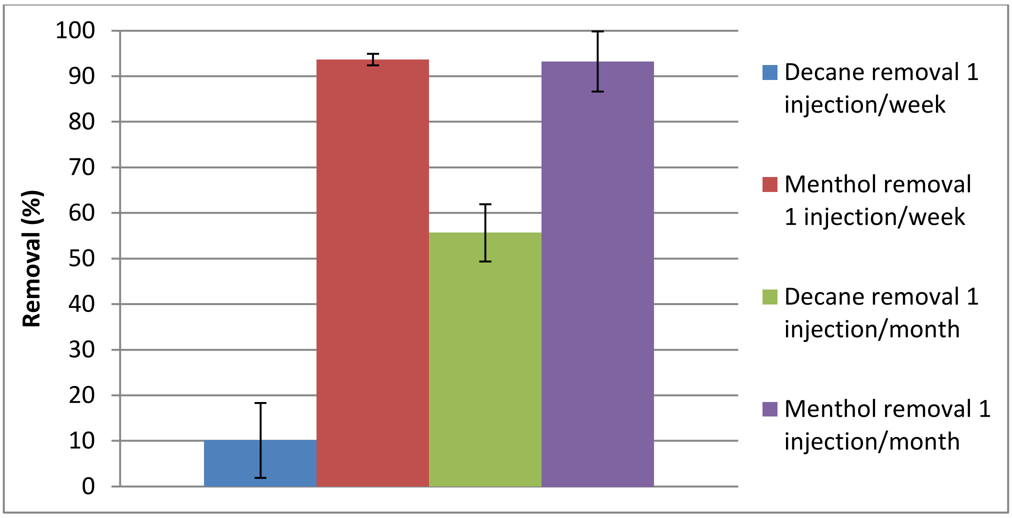


Fig.4. Removal rate obtained after treatment by activated persulfate by iron (II)

Fenton's reagent was produced on the column by injection on slot of the tow solutions constituting the oxidants. In first experience, solutions of hydrogen peroxyde and iron (II) were alternatively injected every 15 minutes. Decane was removed of 0% and menthol was removed of 83% (Fig.5). In the second experience, the slot used was 3 min. Decane and menthol were removed of 44% and 90% respectively (Fig.5). The first study made on Fenton's reagent with distant slot has shown much lower removal than those obtain after treatment by activated persulfate. Removal rate of decane was nil and removal rate of menthol is 83% against 94% obtained after tretment by activated persulfate. A better diffusion of persulfate combined with a weak production of Fenton reagent by distant slot injection mode can explained this result. The injection of two solutions (iron II and hydrogen peroxyde) forming Fenton's reagent with a slot of 15 minutes not allowed an optimized production of this oxidant. With slot more short, diffusion of the two solutions is optimized allowing more production of Fenton's reagent (Fig.6).

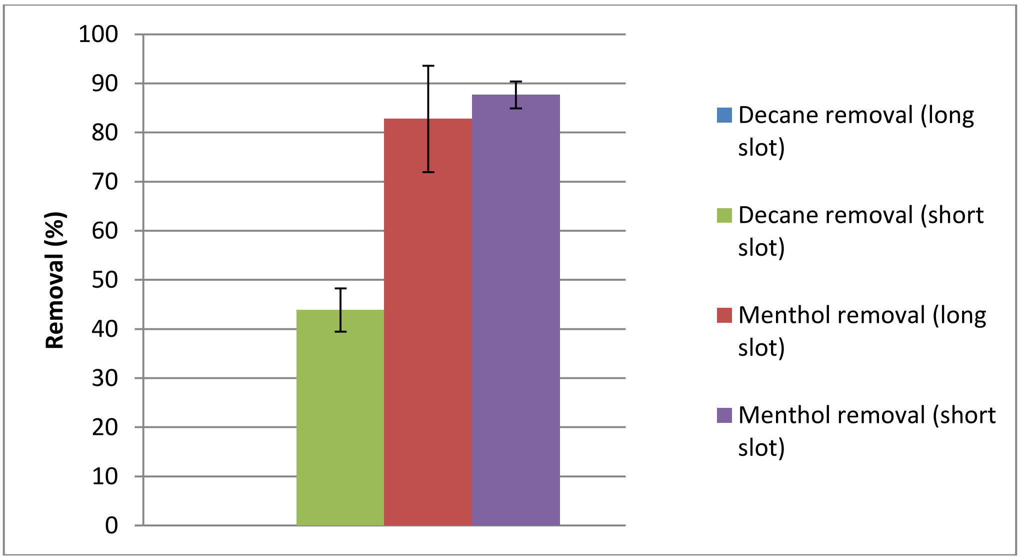


Fig.5. Removal rate obtained after treatment by Fenton's reagent with two slot modes of injection

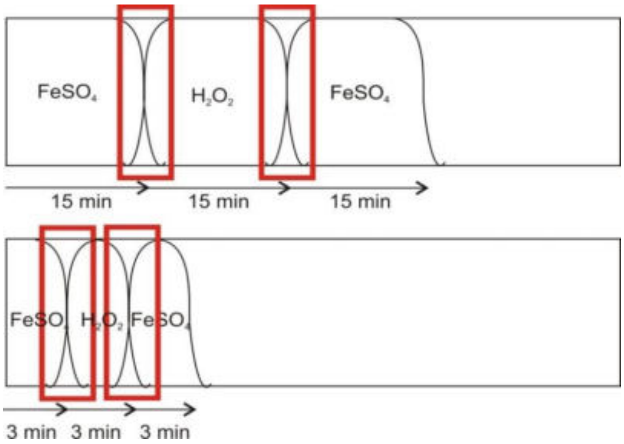


Fig.6. Process of production of Fenton's reagent with two slot modes of injection

Fig.7 shows injection of Tween80 on 20 days. This injection didn't allowe the recuperation of decane. For menthol, 30% was removed after 20 days of treatment. The recovered concentrations in out solutions were consistent with final extraction. Fig.8 shows a study about solubility of menthol and toluene into Tween80 solution. This study was demonstrated the no efficiency of this surfactant onto menthol. The concentraton of menthol solubilized in the Teenw80 solution was 610 mg/L against 450 mg/L in water. This same study on toluene solubility was shown a high solubilization of this compound with Tween80 (1265 mg/L in Tween80 against 500 mg/L in water). This surfactant is more appropriated to the treatment of light hydrocarbon compounds.

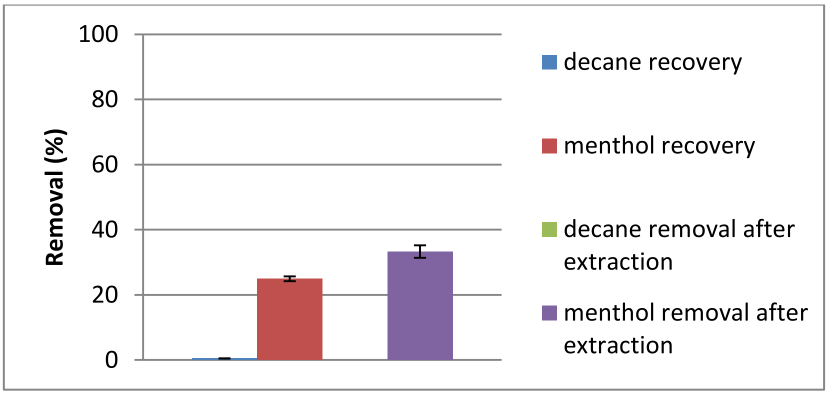


Fig.7. Removal rate obtained after surfactant (Tween80) flushing and pollutants extraction during process

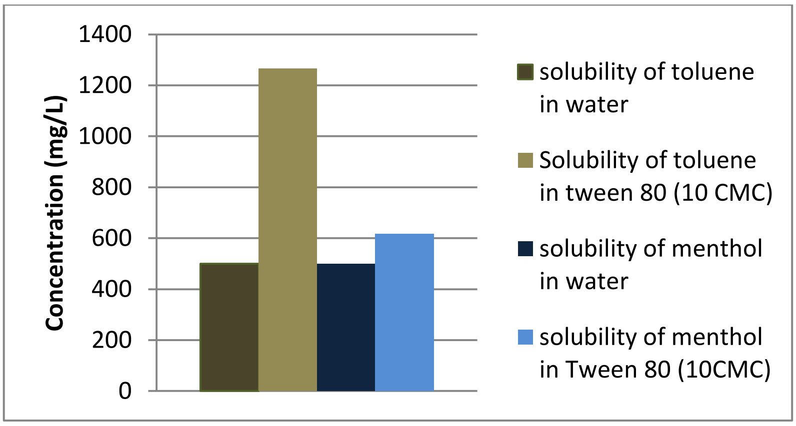


Fig.8. Solubility study of menthol and toluene with and without Tween80

Gaseous injection of air realized on columns polluted by the mixture decane/menthol was removed 59% and 53% of decane and menthol, respectively (Fig.9). The second experience realized on columns polluted by the mixture BTX was removed 91%, 94% and 62%, respectively. Analysis of Tedlar bag connected at the column wasn't shown volatilized pollutants. On columns with BTX, high concentration of benzene, middle of toluene and weak of o-xylene was measured.

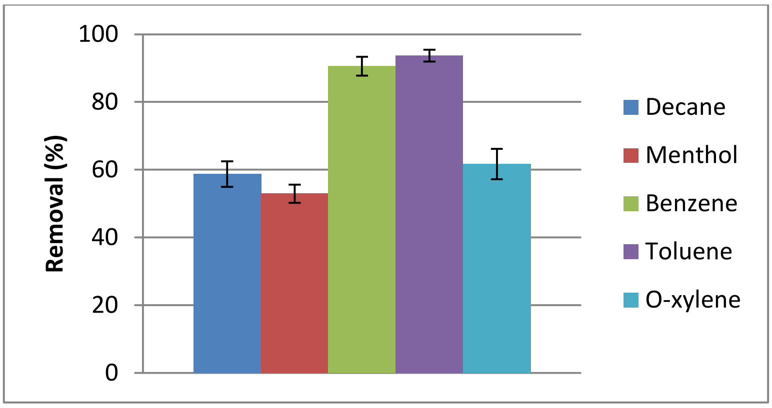


Fig.9. Removal rate obtained after treatment by sparging

Sparging helped to remove 59% of decane and 53% of menthol. Those weak removal rate can be explain by the gazeous injection process of air. The permorfance of gaz into column is not the same as liquid. The presence of preferential passage can explained the gazeous path. In this way, gazeous can't sweep the totality of the column, giving this technic partialy effective.

The experience of sparging realized on BTX was removed more than 90% of benzene and toluene (Fig.9). Those compounds have boiling temperature of 80°C and 110°c respectively, as well as they have a solubility in water of 1,79g/L for benzene and 530 mg/L for toluene. Decane, menthol and o-xylene have higher boiling temperature than benzene and toluene (174°C, 212°C, 144°C), as well as they have water solubility lower than benzene and toluene. Decane is insoluble in water, and menthol and o-xylene have water solubility of 450 mg/L and 175 mg/L respectively. Removal rate obtained with decane, menthol and o-xylene was lower than 70%. Efficiency of this treatment was depended on potential of volatilization and of pollutants water solubility.

Fig.10 shows thermic treatment with a temperature of 80°C applied on decane and menthol. This experience was removed 35% and 15% of decane and menthol, respectively. The same treatment applied on BTX was removed 100% of pollutants. Boiling temperature of decane and menthol are 174°C and 212°C respectively. On these compounds, thermic treatment at 80°C was not efficiency because the volatilization of these compounds was difficult. For BTX, boiling temperatures are 80°C, 110°C and 144°C respectively. Columns heating at 80°C were close to the boiling temperature of BTX provoking a high volatilization of these compounds. The thermic treatment at low temperature is adapted at light hydrocarbon with a low boiling temperature.

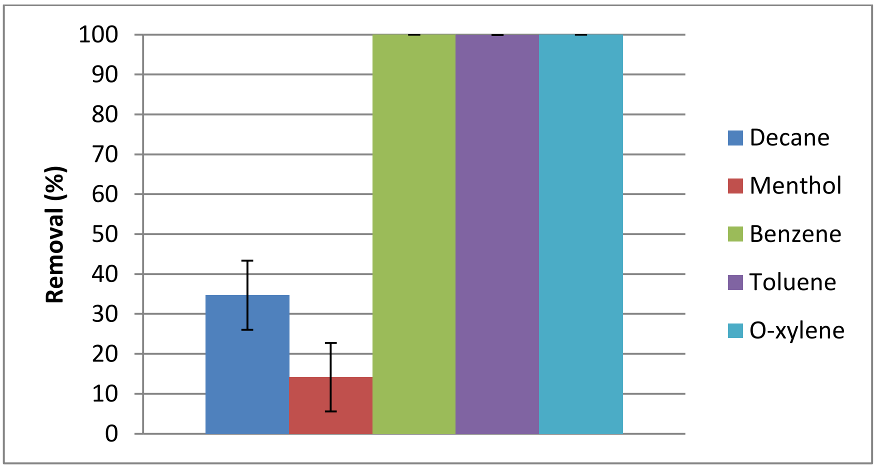


Fig.10. Removal rate obtained after thermic treatment at 80°C

Fig.11 shows oxidation with ozone. This technic was removed 49% of decane and 69% of menthol. Ozone batches were revealed high efficiency of this oxidant to hydrocarbons compounds. For this experience, decane and menthol removal rate were lower than activated persulfate and Fenton's reagent removal rate obtained on columns. This decrease can be explained by the gaseous nature of ozone. Presence of preferential passages didn't permit an optimized contact between pollutants and oxidant. However, removal rate of menthol was higher than that obtained after sparging treatment. This phenomenon can be explained by the higher solubility of ozone than oxygen in water.

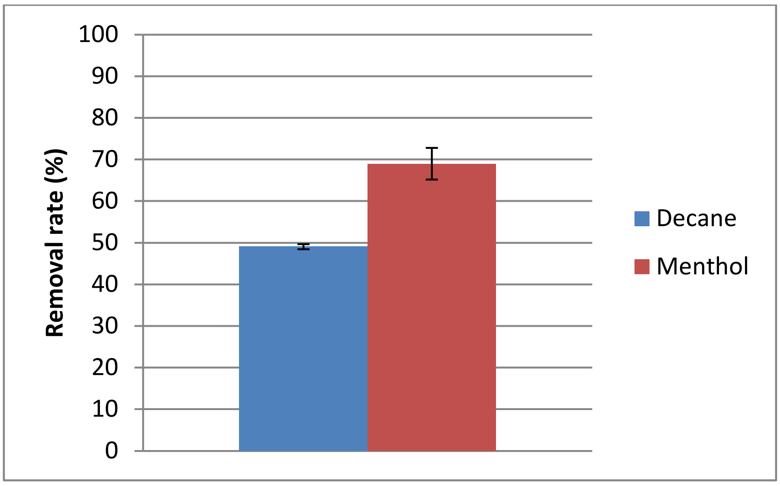


Fig.11. Removal rate obtained after oxidation by ozone

CONCLUSION

The first study on batches showed the absence of efficiency of permanganate toward benzene. This oxidant is thus non-appropriate to treat aromatic rings without alkyl substitution. Known oxidative mechanisms can explain these results. Fenton's reagent and ozone induced a complete removal of BTX compounds within 24 hours of oxidation and persulfate showed the same results within 20 days. All three oxidants treat all BTX very effectively. Except for a slightly higher degradation rate of alkanes by Fenton's reagent, the presence of organic matter plays a minor role on hydrocarbon oxidation. Some differences exist on oxidant consumption by alkanes which is a significant part of the oxidation demand. From that point of view the oxidant that oxidizes the smallest amount of alkanes should be preferred, i.e. persulfate.
The major difference among these oxidants come from their persistency: Fenton and ozone have short half-lives while persulfate remains several weeks to maybe months in natural environments. As it was shown that high oxidant concentrations favor the degradation of BTX compared to alkanes, the major objective will be the distribution of high concentrations over the whole contaminated area. The choice among oxidants will thus mainly depend on the time frame necessary to reach the pollutant source from the injection points and on the potential concentration at this point. It seems that NOD will play a minor role in this process.

Results obtained after experience of columns was showed a better efficiency of technics with liquid injection than gaseous injection. Liquid injection permitted oxidant diffusion through porous media provoking best contact pollutants/oxidants and promoted the elimination of soluble compounds. Injection mode of Fenton's reagent is the factor conditioning optimized production of this oxidant in the column. Surfactant flushing required preliminary study between pollutant/surfactant. In this study, Tween80 didn't permit the solubilization of menthol, whereas toluene was highly solubilized by Tween80. Gas injection didn't permit an optimal diffusion. Only, soluble and volatile compounds were removed. In batches 100% of BTX were removed after treatment by ozone while in columns presence of preferential passages was decreased the removal rate of BTX. Thermic treatment at low temperature was destined to light hydrocarbons like BTX compounds.

Perspective

The third step of this study was the realization of 3D-pilots. These pilots were composed of coarse sand wherein were encapsulated low permeable lenses of sand, polluted by a mixture of toluene and decane, with a saturation of 10%. This experience was realized to compare efficiency of four technics in heterogeneous system. Technics used in this experience were activated persulfate with iron (II), surfactant flushing with Tween80, sparging coupled to ozone and thermic treatment at 70°C.

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SOIL DECONTAMINATION OF POPS BY THERMAL DESORPTION, APPLYING OF THERMAL DESORPTION FOR SOIL DECONTAMINATION PROCESS

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KEYWORDS
Soil treatment, POPs, thermal desorption

GENERAL

Thermal desorption is non-incineration method of soil treatment. This is the way to treat soils contaminated with organic wastes. By heating these soils to temperature 350-800 degrees Cº, contaminants will vaporise and separate from the soil. The vaporised gases are collected and treated in cyclone, oxidiser and bag-house and finally washed by gas scrubber. Vaporised contaminants are destroyed in oxidiser in high temperature 850-1100 degrees Cº (with a gas retention >2 sec). The design has been made according to the EU rules for waste incineration : *REGULATION (EC) No 166/2006 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 18 January 2006 concerning the establishment of a European Pollutant Release and Transfer Register and amending Council Directives 91/689/EEC and 96/61/EC*

Savaterra has six established permits in EU for mobile thermal treatment facility, three in Finland, by one in France, Sweden and Norwegian. In all Savaterra's environmental permits authorities have given following regulations :

1) all treated samples must be analysed by outside independent accredited laboratory,
2) emission (air) must be made similar way.

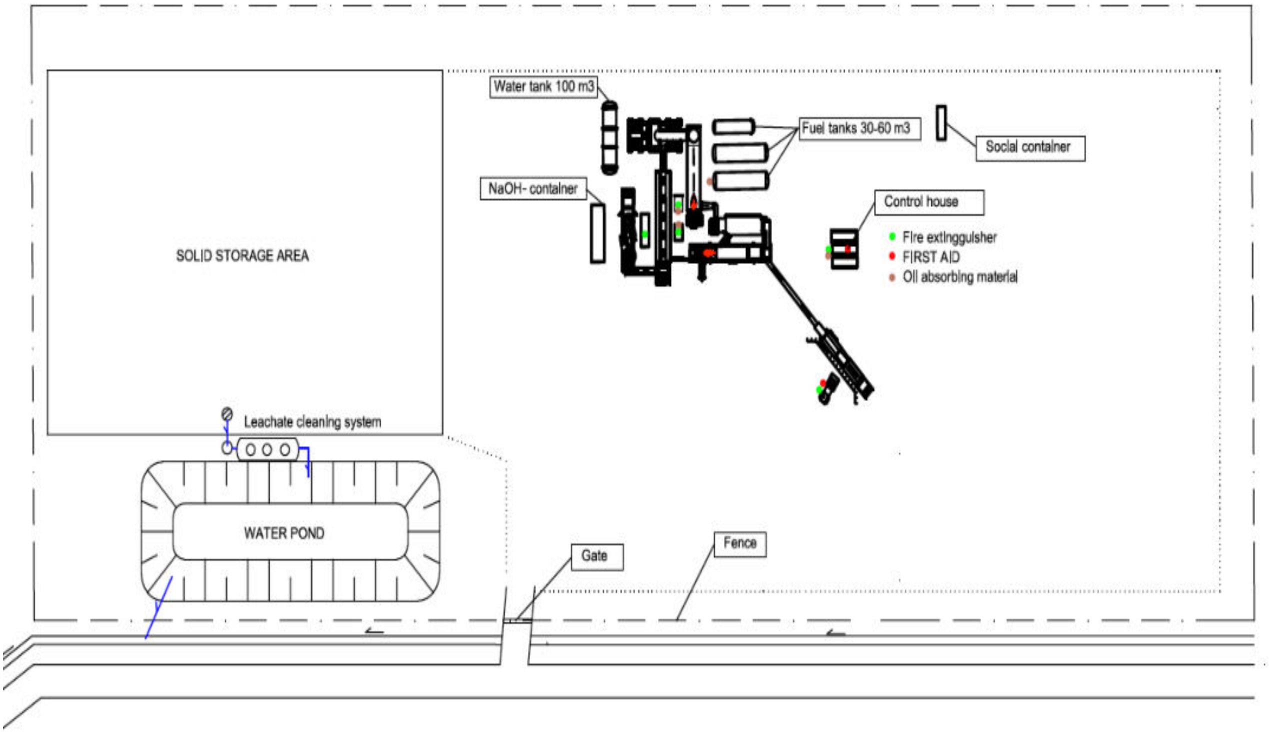


Fig. 1. Site plan layout

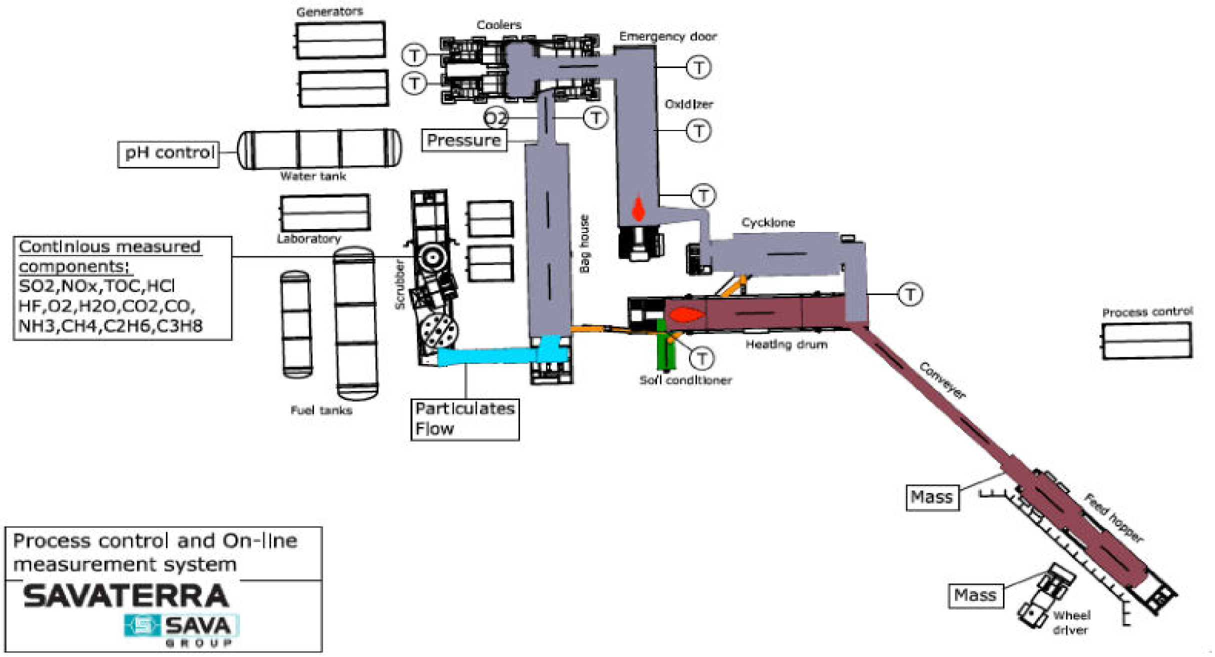
The soil under plant must have good carrying capacity and sustain the wheel loader traffic. The compacting of the soil should be made for 60 ton load. The area needed is about 40 x 50 m.

The water for dust binding and cooling the material will be pumped from water system of the gas washer or directly from water pipe.

The electricity needed in process will be provided by a generator or by normal electric network if available. The thermal desorption plant is made up of unconnected units, which build-up / build-down will take about couple weeks.

The air emissions are monitored by on-line measurements. For the on-line instruments and their measurement points. Periodical measurements carried out by an outside consultant (a certified lab) two times per year. This time also the on-line instruments are tested (calibration functions) by the outside lab.

The on-line instruments are calibrated daily basis according to the manufacturers instructions. The plant can be operated from Monday to Saturday 24h per day.



The on-line instruments are calibrated daily basis according to the manufacturers instructions.

Fig. 2. Measurement system

Gasmet CEMS II

The Gasmet CEMS II FTIR measuring system is designed for continuous emissions monitoring measurements (CEM). Typical application is H_2O, CO_2, CO, N_2O, NO, NO_2, SO_2, HCl, HF, NH_3, CH_4, C_2H_6, C_3H_8, C_2H_4 monitoring from Waste Incinerator or Large Combustion Plants. Measured components and calibration ranges can be changed according to application.

The Gasmet CEMS II is an ideal tool to use for measuring trace concentrations of pollutants in wet, corrosive gas streams. All parts of the Gasmet CEMS II are be heated up to 180 °C. It can be used for undiluted gases and the sample gases do not need drying beforehand.

The Gasmet CEMS II consists of Gasmet FTIR Gas Analyzer, Gasmet industrial computer, Gasmet sampling system. As an option the system can be equipped with Gasmet TDL or ZrO_2 oxygen analyzer and/or with total hydrocarbon analyzer (FID). All parts of the system are 19" rack mounted and are installed on the pull-out shelves. The Gasmet CEMS II includes all power connections and temperature controllers for heated lines and heated sample probe. The operation of the system is fully automatic and controlled by the Calcmet software. Additionally all functions of CEMS II can be controlled manually.

Comprehensive I/O functions make possible to connect CEMS II into all kind of automation or reporting systems. Measuring data and alarms can be transferred from Gasmet CEMS II to other systems with analog or digital format. Gasmet CEMS II is also equipped with analog / digital inputs for external data (other analyzers or process).

Gasmet CEMS II provides different alarm functions such as *System alarm*, *Service request*, *Maintenance on progress* (can be set also manually), *Concentration alarm*, and *Result valid*. Combination for each alarm can be set on Calcmet. If any of the critical alarm is activated, instrument air starts to flow automatically into the system to prevent condensation.

Standard CEMS II is equipped with a two span gas valve to allow automated span/zero checks as required by the new legislation.

Gasmet CEMS II is air conditioned with a compressor-cooling unit on top of the cabinet. Cabinet includes ready made through-leading rubbers on each side and top of the cabinet for all cables and lines. Gasmet CEMS II is also supported by full remote control.

The Gasmet CEMS II FTIR has a very low cost of ownership; the equipment is extremely well designed, and requires very little maintenance. The system also has a number of in-built failsafe devices to protect the instrument from potential damage.

General parameters	
Measuring principle:	FTIR (Fourier Transform Infrared)
Performance:	Simultaneous analysis of up to 50 gas components
Operating temperature:	20 ± 20 °C, non-condensing,
Storage temperature:	-20 - +60 °C
Response time, T_{90}:	< 180 s, 20m heated line
Gas cell temperature:	180 °C
Sample gas:	Non-condensing, particle free
Flow rate:	~ 4 liters per minute
Sample gas pressure:	Ambient
Installation place:	Dust free and clean ambient air, without external vibrations

Fig. 3. Online emission measurement

DUSTHUNTER SP100
Scattered Light Particulate Monitor

Continuous Measurement of Dust with Low to Medium Concentrations

Intended Purpose
The DUSTHUNTER SP100 monitor provides continuous measurement of particulates in industrial plants for process control and PS-11 compliance.

Models
The DUSTHUNTER SP100 (probe version) is available with the following probe lengths:

- 17.13 in (435 mm)
- 28.94 (735 mm)
- 40.75 in (1.035 mm)
- 52.56 in (1.335 mm)

This makes the DUSTHUNTER SP100 ideal for a wide range of applications.

The DUSTHUNTER SP100 consists of the following components:

- DH-SP sender/receiver unit
- Flange with tube
- MCU control unit (with/without purge air supply)
- External purge air unit (option)
- Connection cable
- Purge air hose for MCU-P control unit with integrated purge air supply

Fig. 4. Dust-particles measurement

The operation will take place in two shifts of three men. Sunday is reserved for maintenance work. The plant personnel consist of two operator, one foreman and one wheel loader driver. The personnel fill the daybook of production. Quality and quantity of production, disturbances, maintenance work etc. are written into daybook.

Tab. 1. Measurements of flue gas emissions at the thermal processing unit of contaminated soil on and measurements of flue gas emissions at the thermal processing unit of contaminated soil (heavy metals)

Parameter	**Result**	**Paremeter**	**Result**
Volumetric flow of flue gas (dry fl.gas.)	18,2 m^3n/s	Mercury (reduced O_2 level 11 %)	2µg/m^3n
Flue gas temperature (dry flue gas) after gas washing unit	59°C	Cadmium (reduced O_2 level 11 %)	0,10µg/m^3n
Flue gas humidity (dry flue gas)	19%	Thallium (reduced O_2 level 11 %)	<0.01µg/m^3n
O_2 (dry gas)	13,6%	Antimony (reduced O_2 level 11 %)	0.001µg/m^3n
CO_2 (dry gas)	6,0%	Arsenic (reduced O_2 level 11 %)	0,01µg/m^3n
CO (dry gas)	0.0006%	Cobalt (reduced O_2 level 11 %)	2µg/m^3n
CO (reduced O_2 level 11 %)	11mg/m^3n	Chromium (reduced O_2 level 11 %)	0,3µg/m^3n
SO_2 (reduced O_2 level 11 %)	5mg/m^3n	Copper (reduced O_2 level 11 %)	0,8µg/m^3n
NO_X (reduced O_2 level 11 %)	111mg/m^3n	Lead (reduced O_2 level 11 %)	0,1µg/m^3n
TOC (reduced O_2 level 11 %)	6mg/m^3n	Manganese (reduced O_2 level 11 %)	0,5µg/m^3n
Solids (reduced O_2 level 11 %)	7mg/m^3n	Nickel (reduced O_2 level 11 %)	0,4µg/m^3n
		Vanadium (reduced O_2 level 11 %)	0,04µg/m^3

The total concentration obtained in dioxin and furan (I-TEQ) measurements was 0.003 ng/m^3N reduced to the oxygen level of 11%.

PROCESS DESCRIPTION

The thermal desorption plant will be transported the nearness of remediation site. Contaminated soils are excavated and transported to plant.

Description of parts:
1.Feed hopper - The wheel loader unloads the contaminated soils to **feed hopper** where material larger than 150 mm in diameter are removed. Larger material will be crushed and recycled into the feed or delivered to landfill. The capacity is adjusted in feed hopper according the concentration and quality of contaminant. If contaminated soil is very wet or has a lot contamination, it may need to be mixed with less contaminated or workable soil for treatment in desorption unit. Metal material will be removed by **magnetic** after feed hopper. **A conveyor belt (2)** will load the material into desorption unit.
3.Desorption unit - The desorption unit is used to heat contaminated soil to a high enough temperature and for a long enough time to dry it and vaporize the contaminants from soil. The unit is a rotary desorber which has a rotating ,cylindrical metal drum. The rotation speed and the angle of the drum will adjust treatment rate (tons/hour) Temperature in the drum can be adjusted in the range of 350-800°C depending on the contaminant. Typical retention time of the material in the desorption drum is approx.. 20 minutes. The desorber has direct flame in the oven. This means that the material has direct contact to flame. The material can heat up to 1000°C. Oven will always have under-pressure. **4.Cyclone** - As the soil is heated, the contaminants will vaporize and become a part of gas stream of air which is caused by blowers. Gas flow from desorber is guided by under-pressure to cyclone where most of the particulate matter will be removed.
5. Afterburner - After cyclone, vaporized contaminants will be burned in an afterburner (oxidizer). Temperature 850-1100 degrees C° destroys the contaminants in to CO_2. **6. Heat exchanger** - The flue gas is cooled to 180°C before entering the bag house. **7. Bag house** takes away most of particles. Activated carbon can be utilized in the bag house to remove Hg from the flue gases. **14. Gas scrubber** is connected to process if sulphur (SO_x) concentration in soil or fuel is exceptional high level. SO_x will react with water and sodium hydroxide as follows:

$$SO_2 + 2\,NaOH \rightarrow Na_2SO_3 + H_2O$$

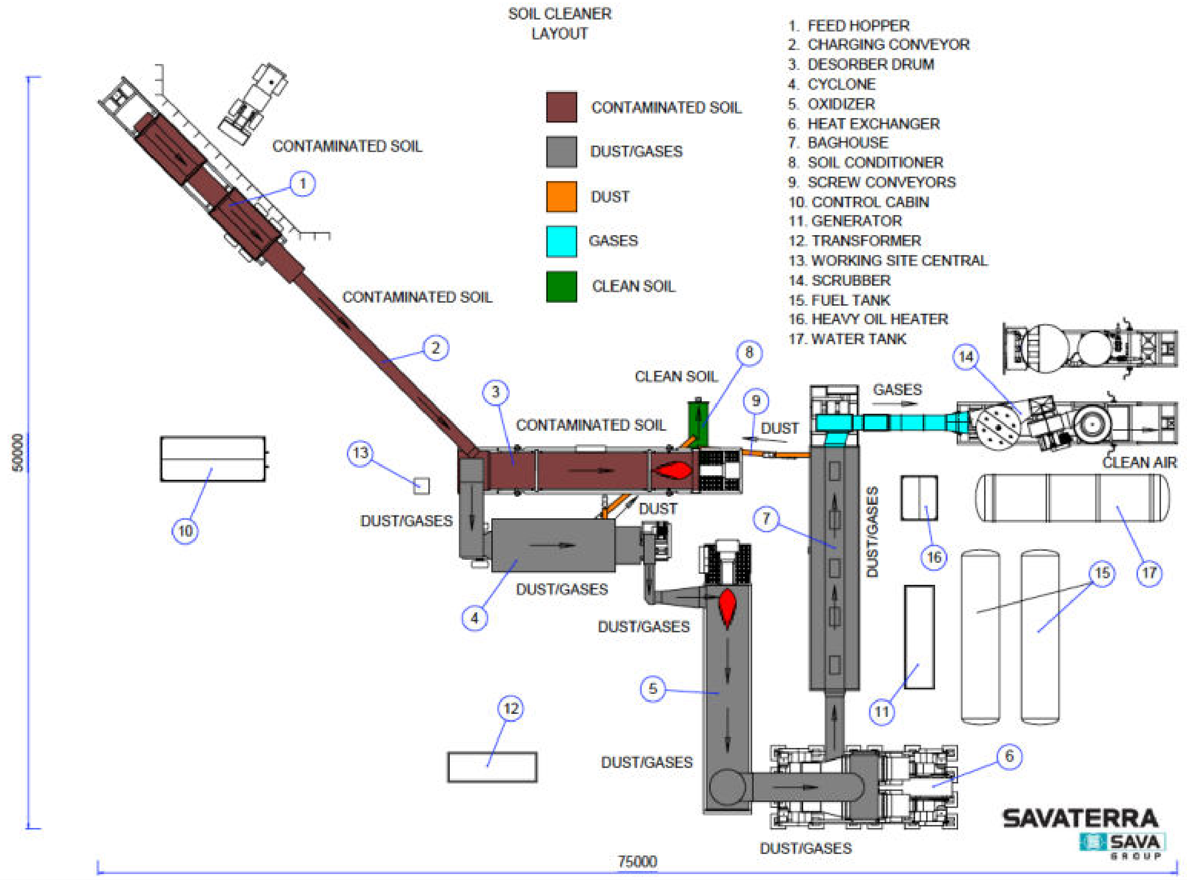


Fig. 5. Thermal desorption layout

Scrubber also helps to remove last particles. Water of the scrubber will be treated in water treatment process and re-used in dust binging of soil. Gas washing unit will also take some nitric oxides :

$2\ NO_2 + H_2O \rightarrow HNO_2 + HNO_3$
$3\ HNO_2 \rightarrow HNO_3 + 2\ NO + H_2O$
$4\ NO + 3\ O_2 + 2\ H_2O \rightarrow 4\ HNO_3$
$4\ NO_2 + 2\ H_2O + O_2 \rightarrow 4\ HNO_3$

In the gas washer nitric acid will form:

$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$

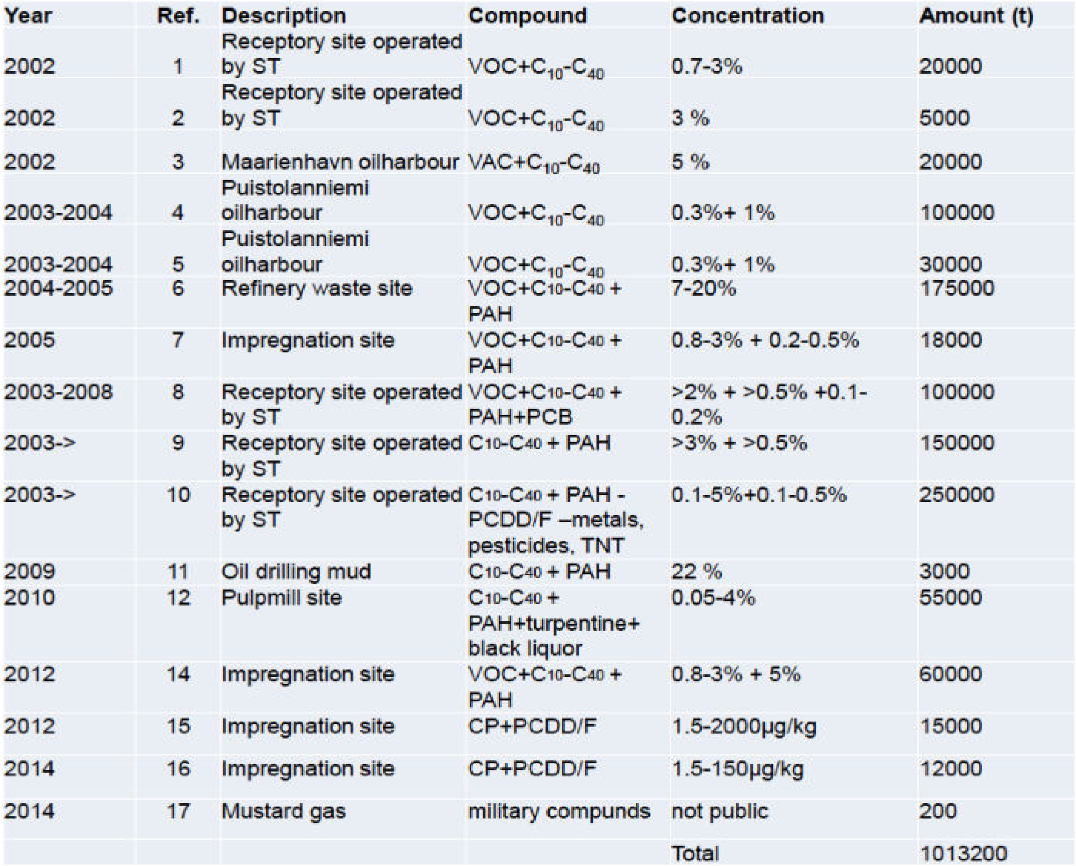
However, in prevention of most of the nitric oxide formation has been done by optimization of treatment temperatures and by adjustment of the burners. Water in the process (steam) will also reduce nitric oxide emission. The gas scrubber will also neutralize possible HF and HCl emissions as follows:

$HCl + NaOH \rightarrow NaCl + H_2O$
$HF + NaOH \rightarrow NaF + H_2O$

Tab. 2. Contaminants, temperature of desorption, oxidation, input and output content of contaminant in soil

Contaminant	Temperature of desorption/ boiling point	Temperature of oxidation	Content of contaminant in soil in input - before	Content of contaminant in soil in output -after
SemiVOC	200-300°C	850°C	<80.000mg/kg	0,02-10mg/kg
PAH	>400°C	850°C	<20-30g/kg	<5mg/kg
PCB	>500°C	>1000°C	<10.000mg/kg	<0,5mg/kg
Pesticides and herbicides	200-300°C	850°C	<10.000mg/kg	Less than detection limit
VOC	200-300°C	850°C	<80.000mg/kg	0,02-10mg/kg
Total hydrocarbons TOC	200-400°C	850°C	<80.000mg/kg	<50mg/kg
Chlorophenols (CP)	>400°C	850°C	<10.000mg/kg	<5mg/kg
PCDD/Fs	>600°C	>1000°C	<1.000mg/kg*	<0,00005mg/kg
Cyanid's (CN)	>400°C	850°C	<40.000mg/kg	<10mg/kg
Metals of 12.groups table of elements (f.e. Mercury Hg)(volatile metals)	>400°C	850°C	<10.000mg/kg	0,005mg/kg
Heavy metals	>400°C	850°C	<10.000mg/kg	Insoluble Salt

Tab. 3. Savaterra Oy references in soil treatment



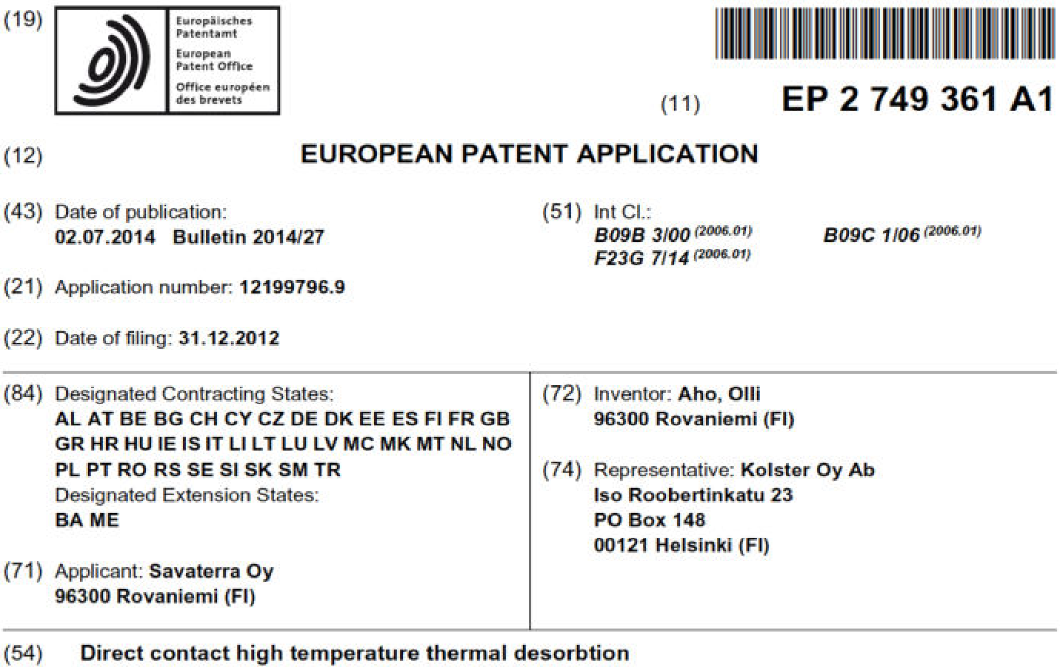
Year	Ref.	Description	Compound	Concentration	Amount (t)
2002	1	Receptory site operated by ST	VOC+C_{10}-C_{40}	0.7-3%	20000
2002	2	Receptory site operated by ST	VOC+C_{10}-C_{40}	3 %	5000
2002	3	Maarienhavn oilharbour	VAC+C_{10}-C_{40}	5 %	20000
2003-2004	4	Puistolanniemi oilharbour	VOC+C_{10}-C_{40}	0.3%+ 1%	100000
2003-2004	5	Puistolanniemi oilharbour	VOC+C_{10}-C_{40}	0.3%+ 1%	30000
2004-2005	6	Refinery waste site	VOC+C_{10}-C_{40} + PAH	7-20%	175000
2005	7	Impregnation site	VOC+C_{10}-C_{40} + PAH	0.8-3% + 0.2-0.5%	18000
2003-2008	8	Receptory site operated by ST	VOC+C_{10}-C_{40} + PAH+PCB	>2% + >0.5% +0.1-0.2%	100000
2003->	9	Receptory site operated by ST	C_{10}-C_{40} + PAH	>3% + >0.5%	150000
2003->	10	Receptory site operated by ST	C_{10}-C_{40} + PAH -PCDD/F –metals, pesticides, TNT	0.1-5%+0.1-0.5%	250000
2009	11	Oil drilling mud	C_{10}-C_{40} + PAH	22 %	3000
2010	12	Pulpmill site	C_{10}-C_{40} + PAH+turpentine+ black liquor	0.05-4%	55000
2012	14	Impregnation site	VOC+C_{10}-C_{40} + PAH	0.8-3% + 5%	60000
2012	15	Impregnation site	CP+PCDD/F	1.5-2000µg/kg	15000
2014	16	Impregnation site	CP+PCDD/F	1.5-150µg/kg	12000
2014	17	Mustard gas	military compunds	not public	200
				Total	1013200

Fig. 6. SAVATERRA'S EVO1 in Chambly France

Tab. 4. Capacity of EVO 1

Technology	Daily capacity (t/day)	Short time capacity (t/hour)	Monthly production (tons)	Yearly capacity (tons)
Thermal treatment of contaminated soils by EVO 1	350	80	7 000 -16 000	84 000- 200 000

Fig. 7. Extract from Patent office register



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(54) **Direct contact high temperature thermal desorbtion**

THE REMEDIATION OF THE EAST TIP, CORK HARBOUR, IRELAND

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KEYWORDS
Steelworks waste, slag, contamination, risk assessment, remediation, ECJ.

ABSTRACT

In August 2011 Cork County Council, on behalf of the Irish State, embarked on a programme for the rehabilitation of the East Tip, Haulbowline Island, Co. Cork. The objective is to address the legacy associated with the disposal of steelwork's waste on a sand spit in Cork Harbour over a 40 year period through the remediation of the site and it's transformation into a public recreational amenity for the beneficial use of the local communities.

Whilst the regularisation process was initiated on foot of a European Court of Justice judgement (ECJ494/01) and associated Letter of Formal Notice [C(2010)6536] the Irish State is committed to ensuring that the remedial solution and amenity development are completed in accordance with current relevant national and international best practice and guidance.

The design of the remedial solution for the East Tip and the preparation of the various application documents (i.e. Planning Application, Waste Licence Application and Foreshore Licence Application) was predicated on the findings of the Detailed Quantitative Risk Assessment (DQRA) - it's function being the quantification of risk to human health and the environment posed by the site and the identification of the remedial solution pertinent to the mitigation of those risks – this in turn was informed by the results of a comprehensive site investigation. Planning permission for the proposed design solution was granted on May 1st 2014 and a waste licence was granted on the 19th June 2014. Further information on the project is available in the Latest News section of the project website www.corkcoco.ie/haulbowline.

INTRODUCTION

Cork County Council has been appointed as Agent for the Minister for Agriculture, Food and the Marine to oversee the regularisation of the East Tip on Haulbowline in order to fulfil the State's obligations under the Waste Framework Directive and address the related shortcomings identified in the Letter of Formal Notice issued in September 2010 [C(2010)6536].

Haulbowline Island is the base of the Irish Naval Service and was the location of Ireland's only steelworks which operated on the Island between 1939 and 2001. Waste from the steel production process was deposited on the Spit Bank, a shallow sand spit extending eastwards from the Island, from the early 1960's. This area of reclaimed foreshore which is 9ha (22 acres) in area and contains approximately 650,000m^3 of waste became known as the East Tip (Figure 1). The waste mass has been estimated to consist of 64% slag, 14% refractories, 13% millscale; 7% scrap, 1% sludge and 1% other wastes including flue dust (0.1%).

A planning application seeking consent to remediate the East Tip and transform it into a public recreational amenity (Figure 2) was submitted to An Bord Pleanála[3] (ABP) and the associated waste licence application was submitted to the Environmental Protection Agency (EPA). Even though the site will never operate as a functioning waste facility the waste licensing process was the appropriate mechanism for the regularisation of the site and for obtaining approval for the works and various processes that have to be undertaken to achieve same. While the majority of the waste material at the site is slag, which is classified as non-hazardous, the presence of some hazardous wastes within the bulk waste mass and mixed within the slag necessitated the application for a hazardous waste licence. A waste licence was subsequently granted and as the remediation will involve works in the foreshore all necessary foreshore consents were also be obtained.

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[3] Irish planning authority

The project has the principles of sustainability at it's core in terms of environmental protection, in terms of social inclusion and enhancement for the wider community and in terms of design and development. The design was predicated on the findings of the Detailed Quantitative Risk Assessment (DQRA).

Fig. 1. Aerial photograph of Haulbowline Island.

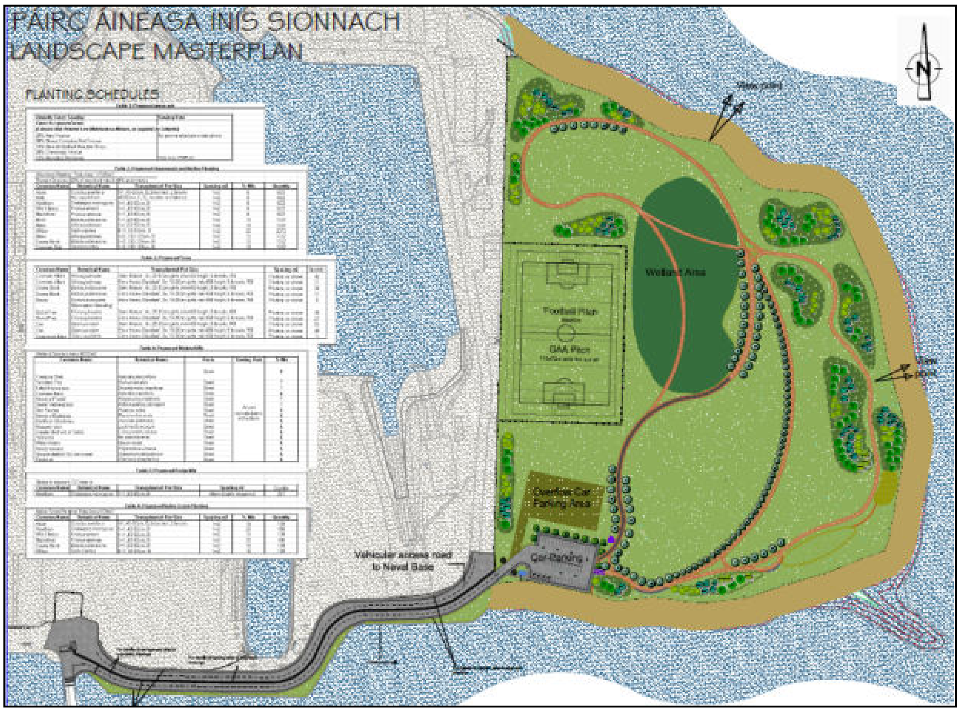

Fig. 2. Proposed public amenity.

DETAILED QUANTITATIVE RISK ASSESSMENT

Aims and Objectives

The overall aim of the DQRA was to provide an assessment of the significance of the risks to human and environmental receptors presented by the waste deposited on the East Tip and identify mitigation measures where appropriate. This required the determination of risk to current site users, to potential users of the proposed public amenity and the determination of both the current and future (post-remediation) risk to groundwater and surface waters. The scope of work included:

- Providing an integrated profile of the chemical and physical nature of made ground, alluvium, gravel and bedrock by defined area;
- Providing a detailed interpretation of testing results from current and previous investigations in respect of sources, pathways and receptors;
- Determining the nature of the vertical and horizontal groundwater flows through the identified strata underlying the site to support contaminant fate transport modelling and risk assessment, hydrogeological assessment, drainage design and structures design for the remedial solution;
- Providing a DQRA using best practice modelling techniques in respect to contaminant transport and human health;
- Providing a final detailed Conceptual Site Model (CSM);
- Providing an outline assessment options for managing risks identified; and
- Providing an outline generic design for remedial option selected as most appropriate.

Desk Study
A review of the results of previous site investigations completed on the East Tip in 1995, 1998, 2005 and 2008 was undertaken in order to prepare an initial CSM and identify data gaps. In addition, the UK's Department of the Environment publication *Industry Profile for Steelworks* (DOE, 1995), which provides information on the processes, material and wastes associated with steelworks, was reviewed and informed the compilation of the initial suite of contaminants of concern. On foot of this it was determined that additional site investigations, sampling, testing and monitoring were necessary and these were completed between April and December 2012. As a result the site is now well characterised from both a contamination and risk perspective with each of the waste types and underlying strata being tested, analysed and monitored. In summary the site investigation and monitoring entailed the:

- Installation of 35 no. boreholes, excavation of 31 no. trial pits and 2 no. slit trenches;
- 7 no. geophysics lines;
- Collection and analysis of 108 no. waste samples, 34 no. natural strata and 23 no. leachability testing samples;
- Collection and analysis of 20 no. offshore marine samples, 23 no. harbour water samples, 8 no. shell fish samples;
- 136 no. groundwater samples, 5 no. surface water samples (from excavations), 9 no. foreshore seepage samples;
- 11 no. ground gas samples and 17 no. rounds of gas monitoring; and,
- Groundwater level monitoring over a 2 month period.

When the density of the site investigations, as highlighted in Figure 3, is considered in the context of *CLR Report number 04 – Sampling Strategies for Contaminated Land* (DOETR, 1994) the predicted hotspot area of 2,860 m^2, which equates to 3% of the total East Tip site area, is considered of acceptable scale from a risk perspective and demonstrates the efficiency of the site investigations.

Generic Quantitative Risk Assessment
In order to identify potential contaminants of concern (pCOC) and assess the human health and environmental risks posed by the waste material and associated groundwater an initial screen of the laboratory results was undertaken using Generic Assessment Criteria (GACs). From a human health perspective the park land use Atrisk GACs, GACs which comply with current Irish Framework Guidance (EPA, 2012) and which were considered appropriate for screening soils based upon the possible future recreational use of the East Tip, were utilised to assess potential risks to future human health receptors. In addition the commercial and industrial land use GACs, derived by the Chartered Institute of Environmental Health and the Land Quality Management Team at the University of Nottingham were utilised as they were considered appropriate in assessing risks to the health of current users of the site.

Where contaminants are present in concentrations that exceed GAC at depths greater than 1m, the probability of human exposure via the direct contact pathways is significantly reduced, leaving inhalation of volatile compounds as the dominant pathway with regard to human health risks. Typically, volatile compounds only.

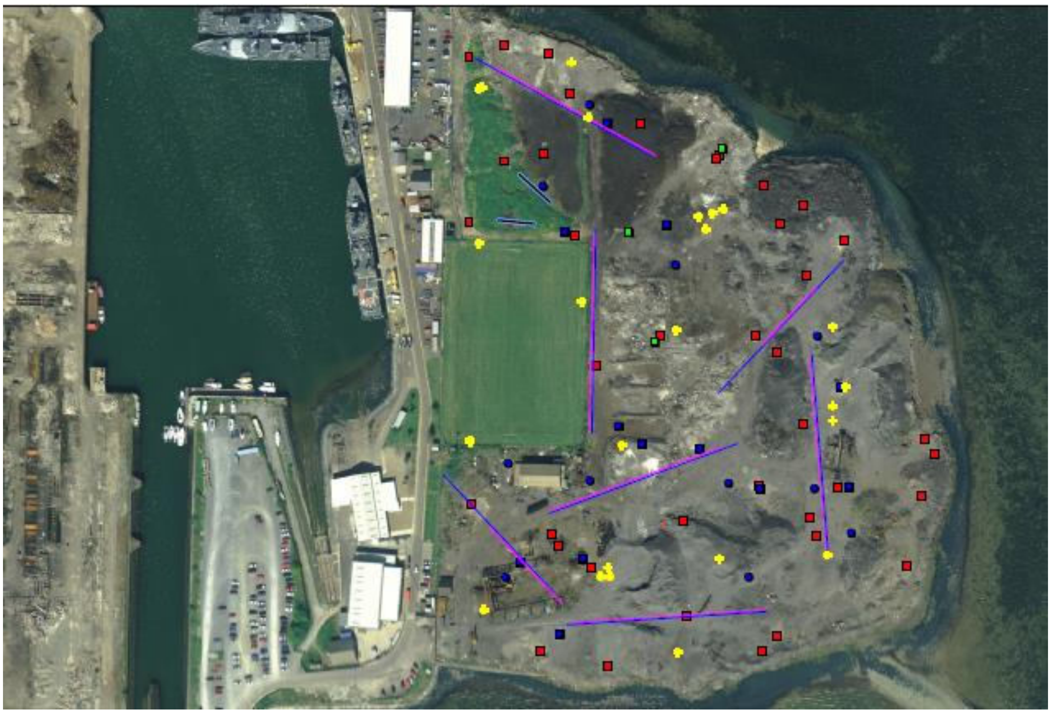

Fig. 3. Site investigation coverage: location of boreholes, trial pits, slit trenches and geophysics lines.

Significantly affect the indoor inhalation pathway. Therefore, for the purposes of considering human health and statistical analysis, data from the top 1.0m has been used for assessment of risks to human health via the direct contact pathway. The comparison of the measured concentrations of the pCOCs against the park land use GACs (Table 1) identifiedthat arsenic, cadmium, lead and vanadium exceeded relevant human health GACs for near surface waste (<1mbgl).

However, potential significant risks to human health have not been identified for concentrations of cadmium and vanadium as the calculated upper confidence level (UCL) 95th percentile mean value did not exceed the critical concentration (park land use GACs). There is sufficient evidence that the likely true mean concentration of the contaminant is less than the critical concentration. An outlier test completed did not identify any potential hotspot areas of higher concentrations for either contaminant. While the 95th percentile mean value did exceed the critical concentration (park land use GACs) for arsenic and lead no potential hotspot for either contaminant was identified. Similarly as the calculated UCL 95th percentile mean concentration did not exceed the critical concentration with respect to commercial land use GACs no significant risks to commercial site users due to the presence of arsenic, cadmium, lead, vanadium have been identified.

The analytical data from solid leachability tests, groundwater and surface water samples were assessed by direct comparison with water quality standards (WQS). Concentrations of heavy metal contaminants in groundwater, particularly in the waste have been measured in excess of WQSs. Risks to human health from metals in groundwater will only occur in two circumstances, if the users of the site can come into direct contact with groundwater or where the groundwater is used for a potable supply. Metal concentrations in groundwater are therefore not of concern with respect to human health. In addition none of the contaminants of concern in groundwater were measured at concentrations which would pose a risk to human health through vapour inhalation pathways and therefore the DQRA has not assessed risk to human health through a groundwater pathway.

Hydrogeological Model

The waste material is heterogeneous in nature with measured hydraulic conductivity rates ranging from a maximum of 2.98 $x10^{-2}$m/s to a minimum of 2.1 $x10^{-7}$m/s. With 60-65% of the overall mass of the waste located below the high tide line the saturated mass of waste material is in a perpetual state of hydraulic interaction with the surrounding tidal waters of the estuary (Figure 3). However, there is a considerable difference in fluctuations in head at the periphery of the site (which are in the order of 2-2.5m) versus

Tab. 1. Statistical Analysis Results for Solid Samples from top 1m – Park Land Use GACs

Contaminant	No. of samples exceeding GAC	Total No. of samples	Park Land Use GAC (mg/kg)	UCL 95th percentile (mg/kg)	95th percentile value exceeds GAC	Outliers	Assessment
Arsenic	8	34	41.4	45	**Yes**	No	**Site wide impact**
Cadmium	1	34	83.6	26	No	No	No impact
Lead	16	34	477	1571	**Yes**	No	**Site wide impact**
Vanadium	1	34	422	333	No	No	No impact

Fluctuations within the interior of the site (which are in the order of 0.5m). Thus it has been determined that there is insufficient time between high and low tide (approximately 6 hours) for the entirety of the leachate within the saturated mass to flow to the periphery before the transient and tidally created hydraulic gradient in one direction is reversed with the incoming tide. The more pronounced tidally influenced fluctuations in hydraulic head near the periphery of the site (i.e. circa 2-2.5m) suggests that a component of flow may be occurring, albeit only for a few hours either side of each high tide and limited with decreasing distance from the shoreline.

Lower contaminant concentrations have been measured in groundwater sampled from depth in natural strata compared to shallow groundwater sampled from waste. It is thus considered that the lower permeable alluvium horizon is inhibiting downward migration together with facilitating attenuation of contaminants. In addition, notwithstanding the tidally induced pressure signal observed in data-loggers, there is no persistent pressure head which could drive advective vertical flow. Consequently, the predominant groundwater migration pathway is laterally through the waste at the periphery of the site and into the Cork Harbour.

Detailed Quantitative Risk Assessment

The flux model has two component parts. The first consists of an estimate of the discharge through the site from each tidal cycle and is based primarily on Darcy's Law which is considered to adequately describe discharge (herein flow) given the inter-granular flow associated with the waste deposits. The second component consists of a calculation of total flux from the site on a daily basis assuming two tidal cycles each day as well as the average daily contribution from precipitation/infiltration.

The dilution model describes a process whereby the daily mixing of a given volume of water (defined by the flux model) containing a given concentration of a particular contaminant (based on representative groundwater chemistry results) is diluted by varying volumes of water in the receptor representing increasing radial distances away from the site within the wider harbour. The model is inherently conservative as it assumes that the water body into which dilution occurs is a static entity, whereas the reality of the situation is that the local system is in a perpetual state of tidally induced flux. Only dilution to the north, east and south is included.

The outputs of the Tier 4 flux and dilution modelling process indicate that there are no theoretical impacts to the waters of Cork Harbour from the majority of the constituents of concern identified by previous tiers of assessment. There is however a theoretical impact to the waters immediately surrounding the shoreline of the site (i.e. within 50m) from chromium (VI) and from manganese but these impacts quickly diminish to negligible concentrations at distances of and beyond 50m of the shoreline. However it should be noted that actual concentrations of these contaminants have not been measured in excess of applicable WQSs for samples collected from the Cork Harbour waters close to the site (between 1-50m) and therefore actual impacts have not been identified. The assessment presented is deliberately conservative having utilised a number of conservative inputs including hydraulic conductivity values, hydraulic gradients and use of mean contaminant concentrations to calculate flux.

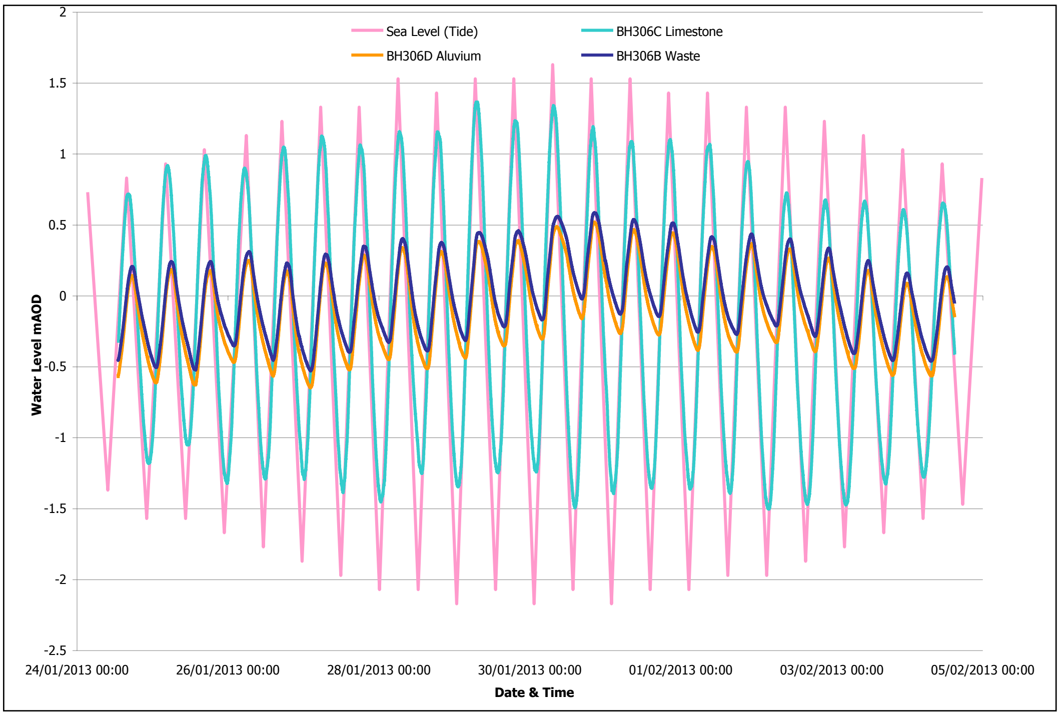

Fig. 4. Hydrograph showing groundwater levels measured in waste, alluvium and limestone.

The outputs of the sensitivity analysis indicate that decreasing the lateral hydraulic conductivity by just one order of magnitude i.e. to 10^{-4}m/s would be sufficient to reduce the theoretical impact of dissolved phase contaminant discharge (Darcy flux) into the harbour to negligible levels and reducing the lateral hydraulic conductivity to 10^{-5}m/s would be sufficient to reduce the impact of the alternative flux calculation scenario.

Conclusions and Recommendations

It was concluded from the DQRA that:

- No risks identified for community; now, during remediation or in long term;
- The site, as it exists, presents a potential health risk to site users;
- Potentially leachable contaminants remain in the waste, albeit at concentrations lower than that already dissolved within the groundwater;
- Groundwater has been impacted with heavy metals and hydrocarbons and is in direct hydraulic continuity with Cork Harbour;
- Highly conservative model predicts theoretical dissolved phase impact in near-shore waters of Cork Harbour although no measurable impact to water observed; and,
- Contaminant contribution from erosion and sediment transport is likely to be more important than dissolved phase flux.

It was thus recommended that:

- The human health risk can be controlled by landscaping and capping;
- Further leachate generation can be controlled by minimising infiltration (i.e. low permeability capping);
- Dissolved phase contaminant loading into Cork Harbour can be controlled by decreasing lateral permeability around the shoreline perimeter of the site in conjunction with low permeability capping;
- Future sediment loading into Cork Harbour can be controlled by creating erosion protection around the shoreline perimeter.

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RED MUD AS MINERAL ADDITIVE TO REDUCE THE TOXICITY OF MARINE DREDGED SEDIMENTS

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KEYWORDS
Red mud, sediment dredging, stabilization, trace metals, ecotoxicity.

ABSTRACT

The contamination of aquatic sediments with metals is a widespread problem. Management of marine dredged sediments is the prime issue in the French Mediterranean coast due to their contamination level. The metal contaminants become available to the surrounding environment due anthropogenic or natural disturbances. Stabilization of pollutants in solid phase with mineral additives is an ex-situ method applied for polluted marine dredged sediments. Present study aimed to assess the potential use of red mud (bauxaline) for decreasing the inherent toxicity of sediment by reducing the availability of pollutants. Red mud has a high pH value which is not suitable for the stabilization of anionic trace elements in dredged sediments. In this study, neutralized red mud is prepared by mixing red mud with 5% of plaster. Then this neutralized product is applied at 5% and 20% rate to assess the leaching of various trace elements (Cu, Cd, Zn, As, Mo, and Cr) in a pilot scale experiment for 3 months from control and stabilized sediment. Results showed a decrease in the availability of trace elements by stabilization with neutralized red mud. Toxicity test are performed against marine rotifers*Brachinous plicatilis*. Red mud is a cost effect choice for remediation of sediments.

INTRODUCTION

Marine sediment pollution is mainly attributed to industrial discharge, shipyard and anthropogenic activities. Recent studies have shown an elevated level of metals (As, Cu, Cd, Zn, Ni and Mo) (Caplat et al. 2005; Schintu et al., 2009; Risso-de Faverney et al., 2010) and organic compounds (PAHs and PCBs) (Andral et el., 2004) and organotins in Mediterranean port sediments (Díez et al., 2002). The problem of contaminated sediments management is closely related to the need of periodical dredging. The dredging of ports is necessary to maintain maritime navigation (Kujala et al., 2010). Currently, in France 50 Million m^3 of sediments are dredged out each year (Alzieu et al., 1999). The polluted sediments are often prohibited to dump back into the sea. Moreover, during dredging the contaminants are remobilized due to excavation and relocation of sediments. The management of the dredged materials complies with the regulations of international OSPAR (1992) and London convention (1972). Thus in France, within the framework for management of dredged sediments, two levels (N1 and N2) were fixed for metals and PCBs. According to these sediment quality guidelines choice of treatment depends on the level of contamination, if the contamination level is below N1 then the sediment is considered uncontaminated with no ecological effects. For this category of sediments offshore dispersal is permitted. Between N1 and N2 level, sediments are classified as contaminated and offshore disposal is prohibited. Sediments are considered highly polluted when they have contaminants level greater than N2. Contaminated and highly contaminated sediments are usually managed on land; hence their management is a great issue due to potential impacts on surrounding environment (Alzieu and Quiniou, 2001). Furthermore, European Council defined leaching limits for inert waste for chemical compounds (e.g. As, Cd, Cu, Cr, Ni, Zn, Mo) to help the authorities for waste management (European Council, 2002). The management of contaminated dredged sediments constitutes a major and challenging problem for European ports. Physical-chemical stabilization is one of the technically and environmentally feasible remediation technique applied for in-situ/ex-situ treatment of contaminants sediments. In this case, the aim of the treatment isto reduce the mobility rather to extract metals. Mineral based treatments were studied for contaminated soil (Kumpiene et al., 2008) and more recently, for contaminated sediments (Peng et al., 2009; Mamindy-Pajany et al., 2013). Mineral amendments were demonstrated to be efficient in stabilizing pollutants in sediments includes iron-bearing materials (e.g. zero valent-iron, goethite, hematite, and ferrihydrite), other adsorbentssuch as alumino-silicates (clays, zeolites) and phosphateminerals (e.g. apatite) (Mamindy-Pajany et al., 2013). Red mud is the by-product of Bayer process. It has a high pH ranging (10-13) value and fine particle size. Due to its fineness and active surface sites it can be used to adsorb anions and heavy metals present in liquid and solid phases (Liu et al., 2011).This removal

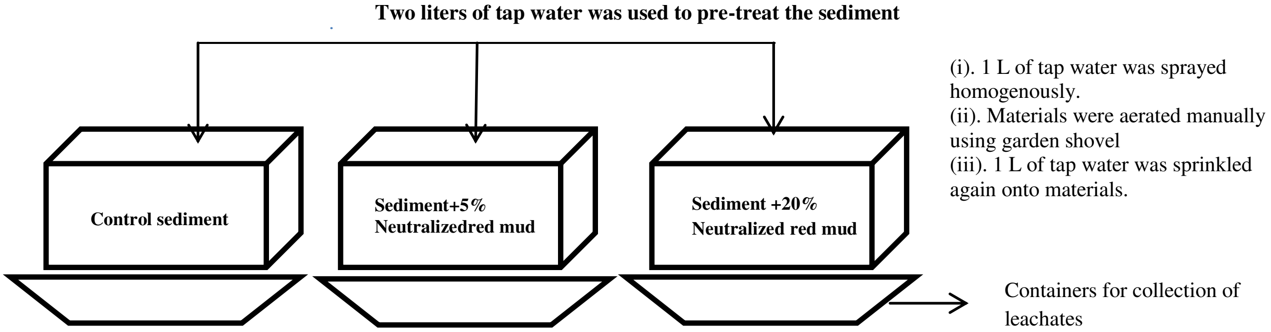
capacity can be increased when red mud is neutralized up to 8.4 to 8.8 pH value (Genç et al., 2003).Red mud was tested as mineral amendment for soil remediation contaminated with heavy metals (Garau et al., 2007; Lombi et al., 2002; Guo et al., 2006),but fewer studies have been reported so far for the stabilization of inorganic pollutants in sediments using mineral additives (Mamindy-Pajany et al., 2013; Peng et al., 2009).
In present study, red mud was neutralized with 5% of plaster (5.88% of gypsum) to increase its sorption capacity for pollutants. Stabilization tests were conducted at two application rate (5 and 20%). The concentration of trace metals leached from the sediment and treated sediment were monitored for 3 months in pilot scale experiment. Binding of pollutants to the mineral amendments can reduce their bioavailability to the surrounding environment and biota. Therefore, leachates were also tested for the toxicity against marine rotifers. This study will be helpful in assessment of environmental impacts of dredged materials after landfill.

MATERIALS AND METHODS

The sediment was collected along Mediterranean coast from French Navy harbour using a Shipek grab. It was actively composted by port authorities for 4 months. ALTEO Gardanne plant, (France) provided Red mud and neutralized bauxaline was prepared by INERIS. Red mud was mixed with 5% Plaster (net content of gypsum 5.88%). This mixture was hydrated and equilibrated for 7 days with Milli-Q and then the slurry was air dried. pH values of sediment and neutralized bauxaline were measured in suspension of (100g/L) using CONSORT pH meter with a combined pH electrode, calibrated using buffer solutions at pH 4.00, 7.01 and 10.00 at room temperature. Electrical conductivities were determined for sediment and red mud suspensions (100g/L) with CRISON EC meter. Cation exchange capacities of solids were measured by hexamminecobalt trichloride method (ISO 23470, 2007). The acid digestion of the sediment and raw bauxaline was carried out according to USEPA method 3050B usinghot plate (DigiPREP HT, SCP Science). Total inorganic pollutants (As, Cd, Cu, Mo, Ni, Cr, and Zn) were determined by ICP-OES (Optima 2000, Perkin Elmer). Toxicity of leachates was tested using Rotoxkit which is purchased from microbiotest Inc., Belgium.

Experimental design and toxicity test

The pilot experiment was conducted in Nice, (France) during May 2014 to July 2014. Three boxes of equal size (40x40x20 cm) each containing 6Kg of sediment were used. Neutralized bauxaline was applied at the rate of 5% and 20% as mineral additive. A square plastic mesh was fixed at the bottom of each box for the collection of leachates. The inner surfaces of the vats were covered with geotextile to limit the loss of fine particles. Leachates were collected 3 and 2 times in the first and second week respectively. Afterwards, this draining and mixing was repeated weekly during 3 months of experiment.



(i). 1 L of tap water was sprayed homogenously.
(ii). Materials were aerated manually using garden shovel
(iii). 1 L of tap water was sprinkled again onto materials.

Fig.1. Experimental setup

After 1h drainage, leachates were then collected in plastic containers placed under each box. Leachates were filtered through (0.45 µm membrane filter) and trace elements concentrations were measured after acidification at 1% with HNO_3 (65%). pH and electrical conductivity were also monitored in leachates.All the leachates collected during 3 months experiment were subjected to toxicity test using marine rotifer (*Brachinous plicatilis*). Toxicity test was performed according to the standard protocol. Hatching of rotifer were placed in test plates in contact with leachates and incubated at 25 ^{0}C in darkness and after 24 and 48 h, number of dead rotifers in each well was counted. Rotifers are considered dead if they do not exhibit any internal or external movement in 5 seconds observation. For the rotifers test to be valid, control mortality in standard seawater (35ppt) must not exceed 10%. For this test, potassium dichromate was used as reference toxicant.

RESULTS AND DISSCUSSION

Characterization of samples

Standard methods were used to characterize the samples. The main physicochemical properties of sediment, red mud and French sediment quality guideline (N1 and N2 level) for trace metals (As, Cd, Cu, Ni, Zn and Cr) are reported in table 1. No level is defined for Mo. Results showed that higher concentrations of As, Cu, Cd, and Zn are present in whole sediment than the permissible limit N2. Except the Ni concentration which is inferior to N1 level. The risk score for sediment was calculated with GEODRISK software (Alzieu and Quiniou, 2001),this score is greater than 2 meaning that this kind of sediment could not be managed offshore. According to the French legislation it requires in shore treatment.

Tab. 1. Physicochemical properties of sediment and Mineral additive

Parameters	Sediment Characteristics	Red mud	Neutralized red mud	N1	N2
pH	8.18	10.57	9		
EC (mS/cm)	7.44	0.915	3.69		
CEC (meq/kg)	105.3	61.8	40		
specific surface area (m^2/g)	3.5	23	19		
Fine particles <63µm (%)	21.8	90	90		
>63–2000µm	61.7	-	-		
As (mg/kg)	150	-	-	25	50
Cd (mg/kg)	4.69	-	-	1.2	2.4
Cu (mg/kg)	1721	-	-	45	90
Mo (mg/kg)	9.08	-	-	-	-
Ni (mg/kg)	27.36	-	-	37	74
Zn (mg/kg)	1869	-	-	276	552
Cr (mg/kg)	59.11	-	-	90	180
Risk score	>2	-	-		

Stabilization of pollutants and decrease in toxicity of sediment

Stabilization of sediment with neutralized red mud resulted in no notable change in sediment pH. The pH values remained constant around 8.2±0.2 due to buffering capacity of sediment. During pilot experiment, a decrease of the electrical conductivities of sediment from 48±0.05 mS/cm to 11±3 mS/cm was noticed in the first 3 weeks. Then it stabilized around 12±3 mS/cm until the end of experiment. Continuous humidification of sediments with repeated leaching make it suitable for landfill by lowering of EC values of leachates. Leached trace metals (Cu, Cd, Zn, As, Cr, and Mo) concentration per kg of sediment were depicted in Figure 2 during the experiment. A rapid increase of metal infiltration occurred during first 3 weeks. During this period, ecological risk is higher when the sediment is treated on land due to labile fraction of elements. A similar behavior was reported for treated sediment with mineral additives (Mamindy-Pajany et al., 2013). Treatment of sediment with neutralized bauxaline altered the rate of metals mobilization as compared to control. Application of 5% neutralized red mud stabilized the bioavailable fraction of trace metals at following rates: Cu (26.5%), Cd (24%), Zn (35%), As (9.63%), Cr (19.1%), and Mo (2.2%). Whereas with 20% neutralized bauxaline addition the releases of trace elements over the control sediment were as follows: Cu (40%), Cd (55%), Zn (71.2%), Mo (11.7%). and As (5.16%). Sediment treated with higher rate of mineral additive clearly indicates that it stabilizes promisingly cationic pollutants (Cu, Cd, Zn) as compared to control sediment. The stable pH of sediment around 8.2 enhanced the sorption cationic pollutants. Hence, the adsorption of cationic species on red mud (mixture of iron and aluminium oxides) is favored at this pH (Apak et al., 1998; Nadarogluet al., 2010). Addition of red mud and lime can increase the pH of heavy metal polluted acidic soil and favored the adsorption of Pb, Cd, and Zn and promoted bacterial abundance and soil enzyme activity (Garau et al., 2007).

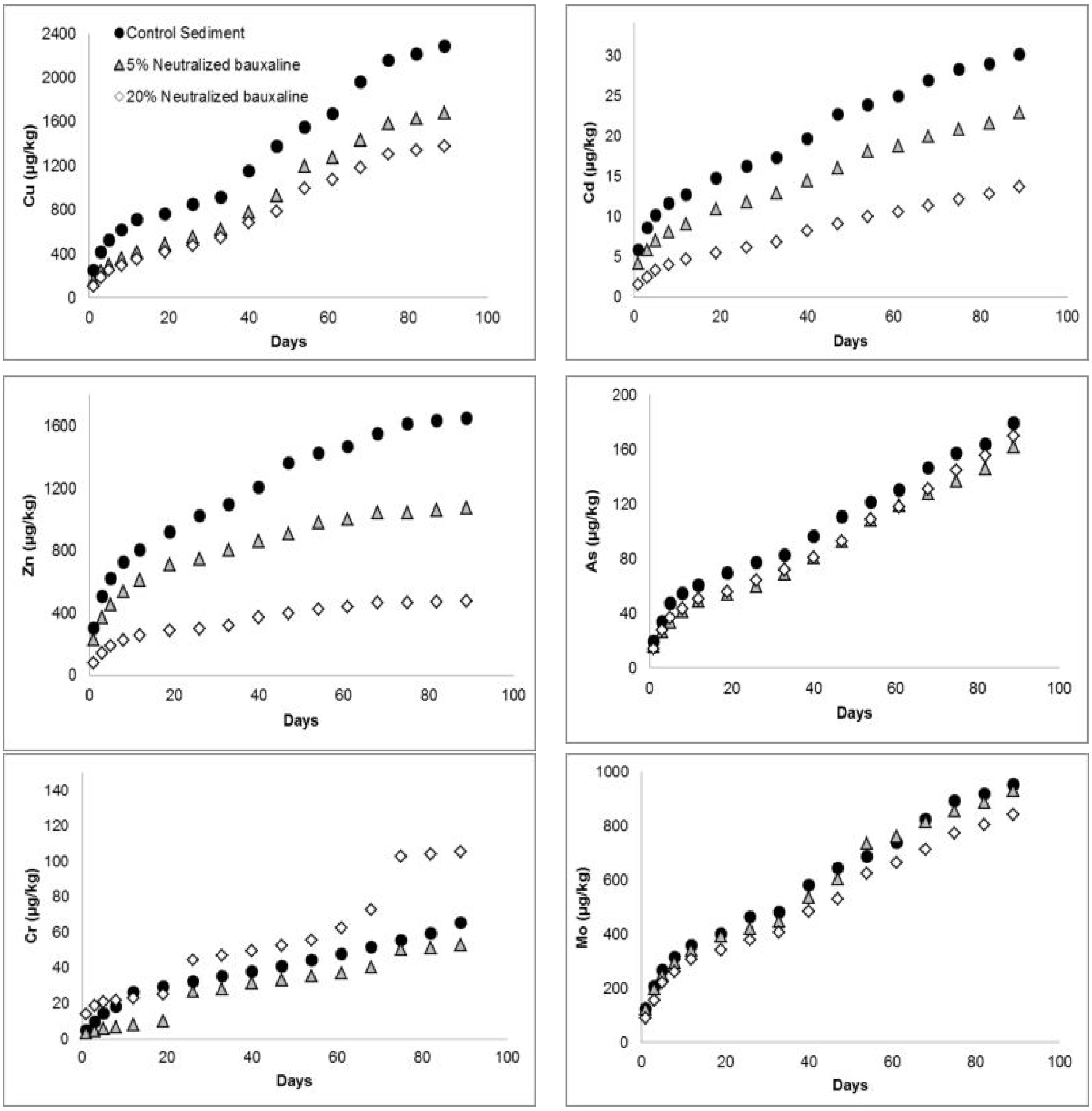


Fig. 2. Quantities of trace elements Cu 2(a), Cd 2(b), Zn 2(c), As 2(d), Cr 2(e) Mo 2(f) released from control and stabilized sediments after 3 months

On the other hand, 5% mineral amended sediment showed a lower rate of immobilization in case of anionic pollutants (As, Cr and Mo) due to higher pH and negatively charged surface of the amendment. However, with 20% additive the rate of stabilization for Mo increased from 2.2 to 11.7%. Previous studies demonstrated that the adsorption of Arsenic, Chromium and Molybdenum is favored on acidic pH (Genç et al., 2003; Goldberg et al., 1996). The pH of sediment matrix is not favorable for the stabilization of anionic species. Higher rate of Cr released from 20% amended sediment is mainly attributed to its concentration found in raw red mud (bauxaline). Moreover, the bioavailable fraction of metals remains low compared to the total metal concentrations in control sediment. Leaching rates of trace elements were calculated on the basis of total concentrations present in dredged sediment (Table 1). The rate for all the pollutants remained lower than 1% except for Mo (10.48%). The rates of trace metal mobilization were also calculated for 5% and 20 % stabilized sediment as compared to their total concentrations in control. The rates were of the same order of magnitude: i.e., inferior to 1% except for Mo (9-10%). Studies conducted on the stabilization of pollutants in polluted sediment have reported higher concentration of leached Mo during field experiments. Process of humidification and successive leaching results in release of amplified quantity of Mo. Molybdenum transformed into water soluble form on air drying and increased leaching was observed (Fox and Doner, 2002; Mamindy-Pajany et al., 2013).

Tab. 2.Comparison of regulatory levels defined for inert waste with metal concentrations (As, Cd, Cu, Zn, Mo, and Cr,) measured in at liquid to solid ratio of 2L/Kg.

	Regulatory levels (µg/kg)	**Control sediment** (µg/kg)	**5% Neutralized red mud** (µg/kg)	**20% Neutralized red mud** (µg/kg)
As	100	69.7	54.2	55.5
Cd	30	14.8	10.9	5.4
Cu	900	762.8	486	417
Zn	2000	921.1	707.8	286.5
Mo	300	401	392	341
Cr	200	29.4	10	25

In Europe, permissible limits are defined for dumping of solid waste on land. In table 2 comparisons of leached metal concentrations during stabilization experiment with regulatory levels is presented for liquid to solid ratio 2. This ratio was achieved in the first three weeks of successive leaching with tap water in pilot study. Addition of mineral additive (red mud) chemically stabilized the pollutants in sediment. Stabilization with 20% amendment is more effective than with 5%. Cr leaching remains within permissible limits irrespective of its concentration in bauxaline. Red mud can be used to as a stabilizing agent to manage the huge quantities of dredged sediment.

Toxicities of leachates samples were presented in table 3. Results showed that there is no toxic effect for shorter contact period of 24h in standard sea water as well as in all the leachates samples. Rate of mortality reached up to 73% after 48h in control sediment. The rates of mortality successively decreased during first three week due to rapid decrease in EC and increased leaching rate of dissolved metal concentrations. After, this period little change in mortalities was observed for all the samples due to lack of nutrients for rotifers growth. Both the treatments found to be effective in reducing toxicity of sediment.

Tab. 3. Average toxicity of all leachates

Mortality (%)	**Standard seawater**	**Control sediment**	**5% Neutralized Red mud**	**20% Neutralized Red mud**
After 24H	0±0	0±0.15	0±0.05	0±0.068
After 48H	0±0	73±0.64	49±1.02	36±0.97

CONCLUSIONS

The polluted marine dredged sediments pose ecological risk due to the leaching of trace elements. Result of pilot study showed that addition of 5% and 20% neutralized red mud to the sediment have no effect on sediment pH but decreased the EC as well as the soluble and extractable metal concentrations in sediment as compared to the control sediment. The bioavailable fraction of Cu, Zn and Cd was effectively stabilized with 20% amendment.Complex matrix of sediment makes it difficult to stabilize all the pollutants. For anionic pollutants, the rate of stabilization does not exceed 10% but both the amendment rates are effective in reducing the toxicity of sediment. Proper neutralization and application rate can make the red mud as an emerging low cost material for inshore treatment of sediment polluted with cationic species. To be significantly effective towards anionic species (As, Mo, Cr), it should be investigated the use of acidic stabilized, since adsorption of anionic species is favoured at acidic pH values. Toxicity of the sediment was significantly reduced after addition of neutralized bauxaline compared with the control. Rotifer test is a rapid and sensitive tool to determine toxicity of marine sediment.

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SORPTION PROPERTIES OF PEAT'S ORGANIC MATTER FOR U AND ^{226}RA, IN MINING AREAS

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KEYWORDS
Uranium, radium, peat, sorption, modeling, ion-exchange, uranium mines

ABSTRACT

The environmental footprint of former uranium mining activities is a major concern for AREVA who is in charge of monitoring these ancient mining sites in France. In order to limit the radiological impact on the biosphere we must have a good knowledge of the chemical properties controlling the migration of uranium U(VI) and its decay products, in particular radium (^{226}Ra).

In the environment, among solid phases which can retain U(VI) and ^{226}Ra, organic matter is known to have a relevant affinity for these radioelements. This is why, wetlands are studied and deployed as mining-water passive treatment solutions. Naturally organic matter is often found as peat. This complex material combines many components in various proportion such as organic compounds (humic and fulvic acids, organic acids, bacteria, fungi) and mineral phases (iron oxy-hydroxides, clay minerals), each having their own specific reactivity and influence on U(VI) and ^{226}Ra behaviour.

This study aims to acquire the sorption properties of U(VI) and ^{226}Ra on natural organic matter from peat according to a predictive and thermodynamic model. Studies about metal sorption on organic matter are usually carried out on humic substances in presence or not of mineral phases (Zeh et al., 1997; Krepelova et al., 2006; Zalina et al., 2010). In our case, we will treat the peat material like other mineral phases, considering that peat reactivity towards metals and other contaminants can be described as an ion-exchanger (Tertre et al., 2009).

MATERIAL AND METHOD

Geological setting and sampling

The studied peat (Les Sagnes peat) is located in the vicinity of the former mining site of Fanay (Limousin, France). This peat is of fluviogeneous and topogeneous type deposit. Situated in the Les Sagnes watershed, this peat is under the influence of waste rock piles located just upstream. Implanted on a granitic bedrock, this peat is acidic and is mainly composed of sphaignes. Three cores were extracted from the peat land. The drill cores designated HS1 and HS2 (hot spots 1 and 2) are both characterized by a relatively significant radiation dose rate (1.0-1.7 µSv/h), approximately eight times higher than the natural background. The peat samples (designated IRS) used for retention experiment correspond to the lowest radiation dose rate area (*i.e.* 0.1-0.2 µSv/h) measured in that peat land. Radiation survey was completed by gamma ray spectrometry along the different profiles (see figure 1).

Natural peat can be subdivided in three main levels, the first one, namely the accrothelm, is located 0-20 cm deep and is generally representative of a relatively immature organic matter. The deepest level (below 40-50 cm), namely the catothelm, corresponds to the most evolved organic matter. Two levels were chosen to carry out sorption experiments reported in this study: an intermediate level (35-45 cm) and a deeper level (75-85 cm). The intermediate level, also called mesotelm, corresponds to the zone of the groundwater table oscillation. This level and a more deeply one (150 cm of depth) are also marked by the presence of grey clayey material. Between the surface and 30 cm of depth, nodules of ochre colour are also observed.

These samples were extracted either with a trowel by slices of 10 cm thick or with a Russian corer for the deepest samples. Samples were stored immediately after the coring, in zipped bags at 5°C.

Physical and chemical characteristics of peat like carbonate content, element percentages of C, H, S, N, water content, ashes percentage and mineralogy were investigated at Poitiers ERM laboratory.

Sorption experiments

Before carrying out the sorption experiments, it is necessary to eliminate the most labile compounds retained in the peat in order to obtain a material which would stay as stable as possible all over the duration of the experiments. Alternate acidic/basic washings eliminate the most labile organic products and metal impurities

(metal oxides, pyrite …). Several protocols with acidic, basic and water washings of different durations were tested through TIC-TOC (Total Inorganic Carbon - Total Organic Carbon) analysis and CEC (Cationic Exchange Capacity) measurement. After washing, peat is conditioned under Na^+ form with 0.3M NaCl at pH 10. CEC is then measured by Na^+ displacement by Cs^+ with 10^{-2} M CsCl.
Adsorption experiments were performed in batchs with a solid/solution ratio of 10 g/L in a 10^{-2} M NaCl electrolyte. Experiments were carried out in the 3-10 pH range, pH were adjusted using suprapur HNO_3, after having added the radiotracers. Samples were spiked with 1.10^{-6} M of U(VI). After shaking (96h), samples were centrifuged (15000 rpm during one hour) and supernatants were analysed by ICP-MS (the detection limit is estimated at 10^{-11} M with an uncertainty of 5%). In order to test reversibility of the ion-exchange reactions, uranium free electrolyte was added to the remaining solid, shaken for a few days and centrifuged. Desorbed U in the supernatant was then analysed by ICP-MS. Similarly prepared samples were spiked with ^{226}Ra solutions from 8.10^{-8} to 10^{-7} M. The adsorption and desorption experiments were carried out in the same way, except that the supernatant ^{226}Ra activity was counted by γ spectrometry (the detection limit is estimated at 10 ± 5 Bq or 1.2 10^{-12} moles).

Ion-exchanger model
An ion-exchanger model was used to describe the chemical reactivity of the peat. This approach has already been described in details in the literature (see for instance Tertre et al., 2009; Reinoso-Maset and Ly, 2014). Considering an ion-exchanger characterized by different negative charged ion-exchange sites (X_i^-), these sites are able to sorb cations, including protons, present in the solutions in contact with the solid. The global charge of the solution and the exchanger with the adsorbed cations is neutral. Each ion-exchange reaction can be written as a function of protons according to the following reaction:

$$m > HX_i + M^{m+} \leftrightarrow mH^+ + > M(X_i)_m \tag{1}$$

This reaction is associated with the corrected selectivity coefficients as follows:

$$K^{*i}_{M^{m+}/H^+} = \frac{[> M(X_i)_m] \cdot [H^+]^m}{[> HX_i]^m \cdot [M^{m+}]} \cdot \frac{\gamma_{H^+}{}^m}{\gamma_{M^{m+}}} \tag{2}$$

where $[> HX_i]$and $[> M(X_i)_m]$ are the concentrations of H^+ and M^{m+} ($mol.kg^{-1}$ of dry solid) sorbed on the i ion-exchange site, and $[H^+]$ and $[M^{m+}]$ are their respective aqueous concentrations ($mol.L^{-1}$). γ_{H^+} and $\gamma_{M^{m+}}$ are the activity coefficients of the aqueous species calculated with the Davies equation. The activity coefficients of the adsorbed species are unknown, but their ratio is expected to be constant.

RESULTS

Elementary analysis
In the studied profile (reference sample), results of elemental analysis indicate a C percentage ranging from 31.1 to 46.6% (of dry peat weight), H ≈ 5%, N ≈ 2% and S from 0.2 to 2.1% (maximum reached at level -30-35 cm depth). The ashes percentage is above 10% with a peak of 40% for level -35-45 cm, which is also the level with the lowest water content (80%). Contrary to usual values observed in peat (Gobat et Portal, 1985), ashes percentages are particularly high and are indicative of a relatively high amount of detrital material, which is respectively of 40 and 20% for the 35-45 cm and 75-85 cm level samples. Major and trace elements were also checked after digestion of dry peat samples by hydrogen peroxide. Elementary analysis confirmed the high proportion of detrital minerals, with 56.8% of SiO_2 in the 35-45 cm level and 36.9% in the 75-85 cm level, 13.6% of Al_2O_3 and 6.2% of Fe_2O_{3total}. Consequently, the loss on ignition is around 17.6% for the upper level while it is around 40% for the deeper one. XRD spectrum on the same digested sample is interpreted as a set of quartz, plagioclase, feldspar, kaolinite and mica typical of granitic context.

γ spectrometry
γ spectrometry measurements were carried out along the different profiles of peat. In the two hot spots HS1 and HS2, total activity of radionuclides (^{234}Th=^{238}U, ^{226}Ra, ^{210}Pb) is relatively constant along the profile (around 50 Bq/g) between the surface and 30 cm of depth, except for some uranium anomalies (^{234}Th peaks) located at the surface and at 30 cm of depth in a zone enriched in nodules of ochre colour. In depth activity is negligible.
In the drill hole of reference, the activity of each radionuclide is inferior to 7 Bq/g except at 20-30 cm of depth where ^{234}Th and ^{226}Ra reach 20 Bq/g.

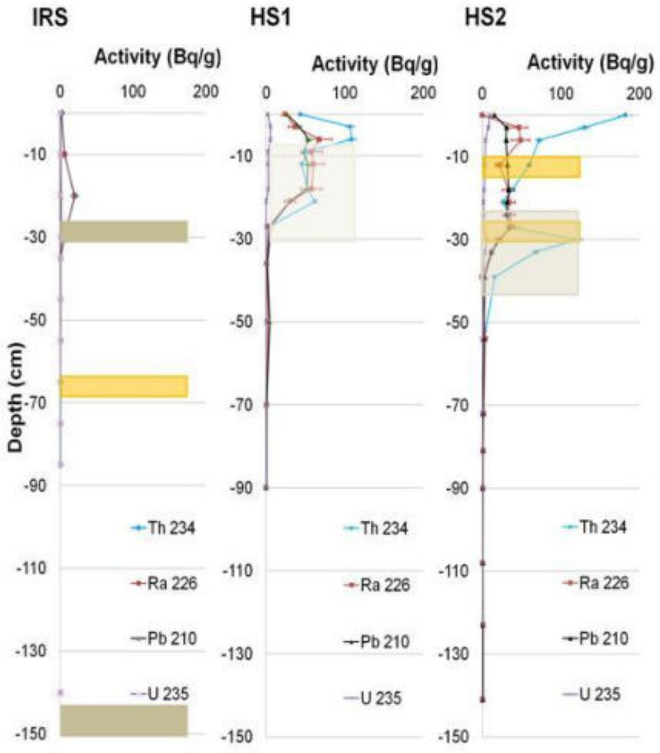

Fig. 1. Profiles of gamma activity of ^{234}Th, ^{226}Ra, ^{210}Pb and ^{235}U in hot spots HS1, HS2 and the reference (IRS). The zones rich in nodules of ochre colour (yellow) and clay layers (brown) are indicated.

U and Ra sorption experiments

Whatever the sample treatment (acid/base washing or water alone), conditioning of the peat material requires *a minima* three weeks of interaction between peat and NaCl electrolyte at pH 10. After conditioning, CEC are comprised between 0.6±0.1 eq/kg of dry peat (35-45 level) and 1.0±0.1 eq/kg (75-85 level). The total organic carbon loss during the treatment of samples is estimated at 30% for the water washing and 40% for the acid/base washing. U background concentration in batchs is evaluated at 10^{-8} M and is taken into account in the mathematical treatment of sorption experiments. ^{226}Ra natural activity is under the limit of detection.

Radioelements adsorption and desorption experimental data are illustrated by the K_d values over pH in figure 2. K_d is the ratio of the adsorbed metal concentration (mol.kg^{-1}) on the aqueous concentration of metal in solution at equilibrium (mol.L^{-1}). Adsorbed U(VI) amount is close to 90% of total U whatever the pH, with K_d values varying from 1000 at pH 3.0 to a maximal value of 10000 mL/g at pH 4.0 (Fig. 2-A). Then the K_d values decrease and stabilize at around 1000 mL/g. The desorption K_d values are slightly higher than the adsorption K_d values attesting that the retention is not completely reversible.

In the case of radium, the percentage of Ra uptake increases from zero at pH 2.5 to 98% at pH 9.6 and above. The associated adsorption K_d values (Fig. 2-B), over the same pH scale, are ranged from zero to 4800 ± 1200 mL/g and seem to remain stable for pH $\geq$ 7. However, in the sample enriched with detrital material (35-45 cm, with blue symbols on Fig. 2-B), the trend of K_d values at acidic pH is slightly shifted towards more alkaline pH.

MODELING AND DISCUSSION

To our knowledge, only a few studies exist about U sorption on organic matter issued from peat bogs (Omar et al., 2007). In this former study, U behaviour is characterized by a maximum U removal from the solution for pH comprised between 4 and 6, which can be related to U speciation over pH. In presence of humic acids (10 mg.L^{-1}), below pH 3.5, U principally remains in solution as UO_2^{2+} but between pH 3.5 and 7.5, formation of uranyl complexes with humic acids seems to be responsible for the highest values of U sorption on peat. At equilibrium with atmospheric p_{CO2}, decrease of U sorption for pH above 7.5 is assigned to the uranyl-carbonate complexes formation.

Assuming that retention is mainly due to the organic fraction closely bond to the solid material, the observed uranium evolution trend has been relatively well reproduced with the model of ion-exchange (see Fig.2-A) considering the sorption of Na^+ and the uranium species on a single site X_i representative of organic compounds such as:

$$> NaX_i + H^+ \leftrightarrow Na^+ + > H(X_i) \quad \text{with} \; K^{*i}_{Na^+/H^+} = \frac{[> H(X_i)]\cdot[Na^+]}{[> NaX_i]\cdot[H^+]}\cdot\frac{\gamma_{Na^+}}{\gamma_{H^+}} \qquad (3)$$

$$2 > NaX_i + UO2^{2+} \leftrightarrow 2Na^+ + > UO2(X_i)_2 \quad \text{with} \; K^{*i}_{Na^+/UO2^{2+}} = \frac{[> UO2(X_i)2]\cdot[Na^+]^2}{[> NaXi]^2\cdot[UO2^{2+}]}\cdot\frac{\gamma_{Na^+}{}^{2}}{\gamma_{UO2^{2+}}} \qquad (4)$$

In the case of trace elements sorption, their concentration in the exchanger being neglected with regards to other species present as major elements, the concentration of X_i (mol/kg) is equal to the sum of the concentration of $[Na(X_i)]$ and $[H(X_i)]$. Therefore, we can deduce from the mass conservation relation and the equations 3 and 4, an expression of the K_d values as a function of the total concentration of site X_i and the constants of selectivity of the different species adsorbed as follows:

$$Kd_{UO2}\cdot[Na^+]^2 = \frac{K^{*i}_{Na^+/UO2^{2+}}\cdot[Xi]^2}{\alpha.(1+K^{*i}_{Na^+/H^+}\cdot[Na^+]^{-1}.\gamma_{Na}10^{-pH})^2}. \qquad (5)$$

α is the Ringbom coefficient (Ringbom and Still, 1972) which relates the total concentration of uranium with the sum of the concentration of the different uranium species, with $U_{total} = \alpha.[UO_2^{+2}]$.

Considering that UO_2^{2+} is the main uranium species present between pH 2 and 5.0, best fitting is obtained with the following selectivity constants: log $K_{Na+/H+} = 2.09$; log $K_{Na+}/_{UO2++} = 1.8$. These values confirm that at acidic pH, carboxylic groups contribute mainly to the natural organic matter reactivity (pKa of carboxylic acids are generally comprised between 3.0 and 4.5). According to the titration curve of peat, the concentration of binding site (X_i) is estimated between 0.2 $mol.kg^{-1}$ of dry peat for the upper sample (35-45 cm) and 0.6 $mol.kg^{-1}$ for the deeper one (75-85 cm).

However, contrary to the former study (Omar et al., 2007) we observe that around 90% of U is still removed from the solution for pH > 8. That phenomenon has already been observed in experimental studies where humic acids are associated to mineral (Krepelova et al., 2006) but is not explained yet.

Therefore, it seems that U behaviour in peat is not only governed by sorption on organic matter. U can also be adsorbed on mineral particles of the detrital fraction (oxy-hydroxide, clay-minerals) and/or controlled by solubility of secondary uranyl-silicate mineral phases. If we cannot exclude precipitation of any silicate phases (such as soddyite or Na-boltwoodite) at medium and alkaline pH, it seems that such a precipitation cannot explain this trend in any case. Simulation with PhreeqC® software (Parkhurst et al., 1999) showed that the contribution of 2% of smectite and less of 1% of iron oxy-hydroxide can explain 90% of U retention in the 7-9 pH range. Such mineral amounts are consistent with XRD characterizations and chemical analyses.

Up to pH 8.0, radium is essentially present in solution under the Ra^{2+} form. The curve of retention of Ra in function of pH can be easily reproduced by ion-exchange reaction on carboxylic type site identified for uranium (see Fig. 2B). Log $K_{Na+/Ra2+}$ is estimated at 0.9. In the case of radium, if we cannot exclude any contribution of clay-minerals and oxy-hydroxide on the radium retention in peat (principally in the more enriched with detrital minerals zone, *e.g.* 35-45 cm level), we can assume that radium is essentially retained by organic component.

This first approach to represent the sorption of radionuclides on a complex natural material with an important organic component showed that it is possible to characterize the chemical reactivity of such a material and to deduce coefficients of selectivity. An operational model has been elaborated to predict the sorption of radium and uranium on peat. It is intended to apply it applied in different environmental situation in order to evaluate its robustness.

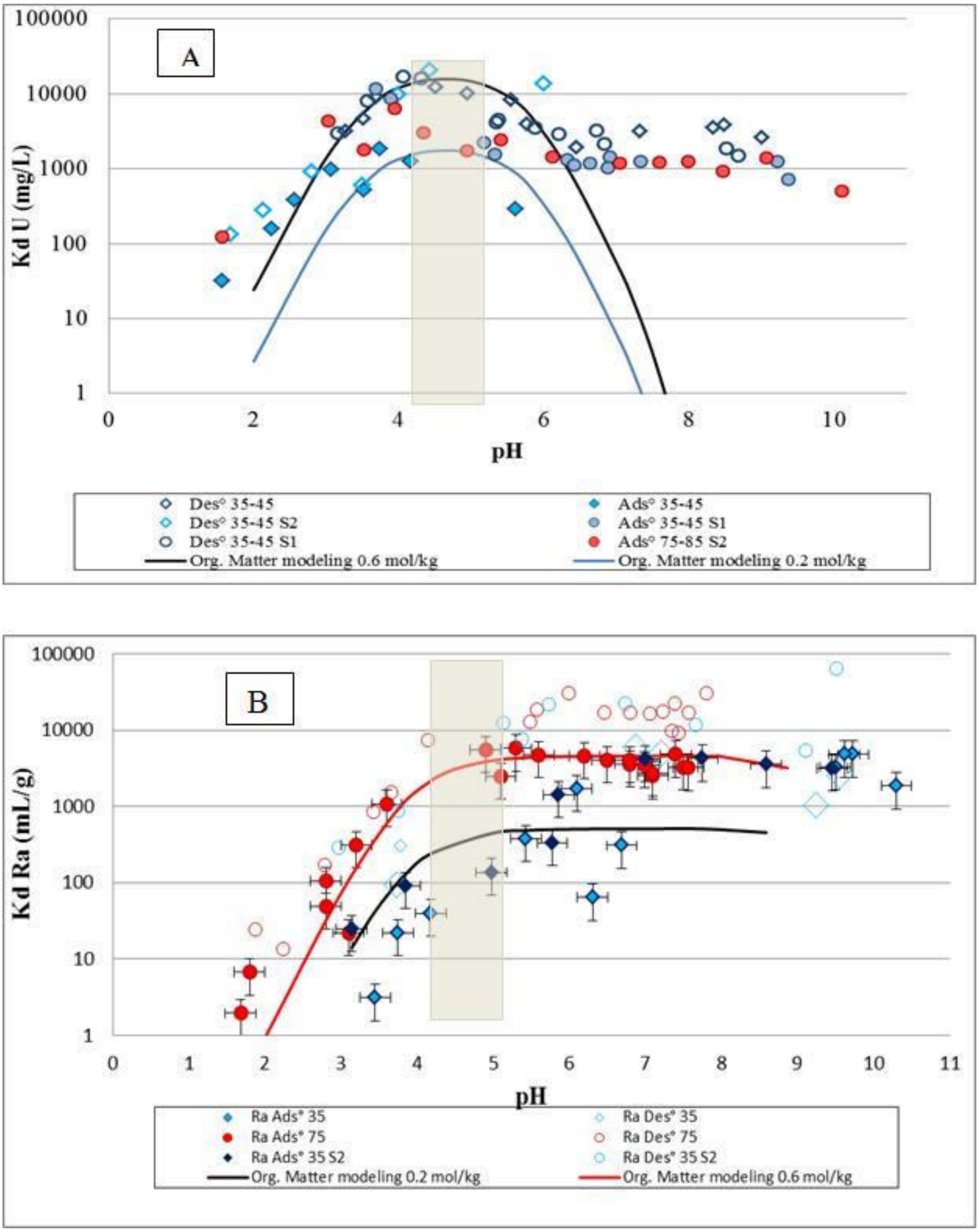

Fig. 2. A- K_d of adsorbed and desorbed U on Les Sagnes peat over pH compared to modeling of retention on the organic component and B- K_d of adsorbed and desorbed ^{226}Ra on Les Sagnes peat over pH compared to modeling of retention on the organic component. Band of grey color is indicative of the *in situ* pH conditions at les Sagnes.

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SOIL HEAVY METAL STABILIZATION BY USING INDONESIA NATURAL ZEOLITE

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KEYWORDS
Soil, heavy metals, stabilization, natural zeolite

This research project was conducted to investigate the effects of a Indonesia natural zeolite for stabilization lead and cadmium contaminated soil. Natural zeolite was added to three contaminated soils. The stabilization of lead and cadmium in soils mixed with zeolite was measured in both column and batch experiments in single and binary system. The result showed that the sorption generally increases with increasing pH for both lead and Cadmium in single metal solution system, while increasing sorption with increasing pH is also observed in the case of binary system. The increasing adsorption capacity with pH under binary system is related to the influence of silanol and aluminol groups that are less protonated with increasing pH and thus more available for the adsorption of the metal ions. This is also supported by the fact that at higher pH active sites on the clay surface is more or less negatively charged and thus promotes cation exchange reactions. Generally, it can be concluded that natural zeolite, as a amendment material, is highly beneficial and suitable especially in both fine andcoarse-textured soils.

INTRODUCTION

Heavy metals are considered as a threat from both environmental and human health standpoints. These metals accumulate in the organisms, thus ultimately entering the food chains. Natural zeolites are plentiful and low cost materials and their cation exchange and molecular sieve characteristics cause them to be as widely used adsorbents. Zeolites are hydrated aluminosilicates high in negative charge due to the occurrence of isomorphous substitution in their tetrahedral lattice and hence they have a strong affinity for the sorption of metal cations. These are inert and non-toxic materials which are appropriate for improving physical properties of soils and amelioration of contaminated soils. These are also ideal for sorption and ion exchange processes (Wang and Peng, 2010). Castaldi et al. (2005) reported that metal retention may occur via cation exchange in zeolites and hence they believed that remediation of soils are mainly affected by CEC. Due to the porous structure, existence of inner and outer charged surfaces and mineralogical heterogeneity the sorption of metals on zeolites is a complex process (Altin et al., 1998).

Sorption of elements is a competitive process between ions in solution and those onto the soil surface. Hence the study of single metal solution has imperfect practical applications (Fontes et al., 2000). Competitive adsorption takes place when two or more metal adsorb to the same adsorption sites (Ryan et al., 2011). The objective of this study was to evaluate the effect of zeolite to remediate Cd and Pb, by using single and binary system, in a variety of soil textures in Yogyakarta with different pH values.

MATERIALS AND METHODS

Zeolite

The zeolite used in this research was obtained from the Gunungkidul District, Yogyakarta Special Province. Geologically, the natural zeolite in study area as part of Kebo-Butak Formation in Southern Mountain region (Yuminti, 2005; Surono 2008).

Soil samples

Uncontaminated soil samples with different textures were obtained from the three different geological backgrounds, in Yogyakarta Province. Contaminated soil samples were prepared by adding 1000 mg/1 CdClsolution to obtain approximately 30 mg/kg of Cd and 80 mg/kg of Pb content respectively. The mixture was stirred up and placed at 25 °C to dry. The samples were ground and water was added until the moisture reached the field capacity level. The wetting and air dry cycle procedure was repeated five times to allow sufficient mixing of cadmium and lead soil to simulate actual field conditions. The procedure also be conducted for making Pb contaminated soil, by using $PbNO_3$ solution.

Experimental methods

Single system

Different portions of zeolite ranging from 1 to 15 g/100 g soil (1, 3, 5, 7, 9, and 15 g/100 g) were added to contaminated soil samples.. The mixtures were subjected to three cycles of the same air dry/rewetting procedure in order to achieve equilibrium. Two different experiments, namely a batch and a column experiment, were carried out.

For the batch extraction experiment, soil mixtures were placed in 150 ml flasks and 100 ml of 0.01 M CaCl solution. Variations of pH were observed in two pH variation. The solution was then shaken for 4 h at a constant temperature of 25 °C and centrifuged at 200 rpm. The solution was then filtered and the filtrate was used for pH and cadmium measurements. The same procedure was conducted for Pb.

The purpose of the column experiment was to simulate and study the Cd and Pb migration in columns filled with a mixture of soil and zeolite. To simulate contaminated soil samples, a height of 20 cm of uncontaminated soil was initially placed at the bottom of a column of 40 cm in diameter, with another 10 cm of Cd and Pb contaminated soil (with or without zeolite) on top of the column. The columns were saturated with a counter flow of deionized water and drained several times in order to release air bubbles in the columns. The soil columns were then submerged in water for a week for saturation. During the experiment, the column was leached using 0.01 M CaCl solution at a constant head of 5 cm. The resulting leachate was collected and analyzed for cadmium and lead concentrations. At the end of the experiment, columns were allowed to drain naturally to determine the water content and soil sample height which were then used to obtain the overall density and pore volume of the columns. The methods used were those described by Potts (1993).

Binary system

Similar with single system, the sama procedure was conducted for Cd and Pb in soil contamination together. The batch and colum test was done similar with previously mention in single system.

Analytical methods

The zeolite size distribution was measured using standard sieves and its CEC value using the indirect ammonium acetate method. Cadmium and lead concentration was determined using an Atomic Absorption Spectrometer (AAS). Soil pH was measured using a pH meter (soil tester).

RESULTS AND DISCUSSION

Experimental result

Soil properties

The result of basicchemical and physical properties of soils are presented in Table 1.

Tab. 1. Several properties of soils samples

Soil	**Particle Size (%)**			**pH**	**Geological background**	**CEC**	**Organic**	**Carbonate**	**Artificial metal concentration (mg/kg)**	
	Sand	Silt	Clay						Cd	Pb
A	60	10	15	3.46	Volcanic	8.91	2.8	0.04 %	31	85
B	10	15	65	7.22	Limestone	51.61	3.5	56.75 %	29	80
C	45	25	20	5.56	Carbonate Sandstone	22.15	2.6	45.65 %	30	70

Single system

The patterns of metal adsorbed on zeolite at different initial concentration of single system are presented in figure 1. For all initial concentrations the amount of metals adsorbed was the highest for Pb followed by Cd, respectively.

In this experiment, different amounts of zeolite were mixed with three Pb and Cd-contaminated soil samples with two pH variation. The change in Pb and Cd concentration in the leachate indicated that zeolite enhanced the sorption capacity of the soil (Figure. 1). The influence of pH was also shown, as the lower pH showed the higher sorption capacity in soil.The addition of natural zeolite strongly inhibited the leaching of cadmium in all the soil samples (Figure 2). Shanbleh and Kharabsheh (1996) showed that when natural zeolite (approximately 35% active faujasite and phillipsite) was added to a soil contaminated with mixtures of Pb^{+2} and Ni^{+2}, the concentration of metals in leachate drastically reduced while the sorption capacity of the soil increased. Leachate Pb and Cd concentration of all three soil samples dropped after was added to contaminated soil sample.

Figure 1 further illustrates that the cadmium concentration reaches a plateau after a critical amount of zeolite is applied. The optimum level of zeolite for soil A, B and C was approximately 9 g/100 g soil.

However, figure 1 further illustrates that the Pb concentration in soil A drastically drop after a 1% amount of zeolite is applied. This differences show that the application pf zeolite was very good for Pb contaminated soil.

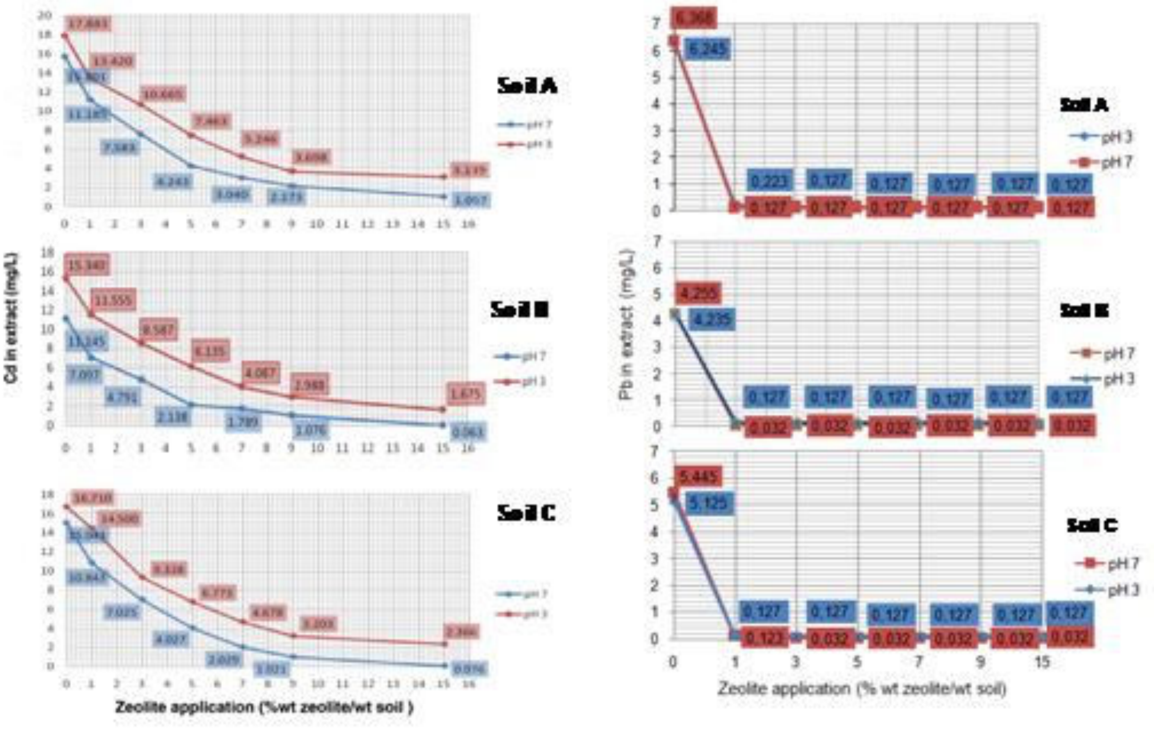

Fig. 1. Leachate of Pb and Cd concentration from simulated contaminated soils as a function of the zeolite dosage.

The results obtained from the column experiments of two loamy soils demonstrated that column in soil C with no zeolite began to have Cd leachates after 2.1 pore volumes of the $CaCl_2$ solution was reached (Figure. 2) while Cd was not detected in the leachate from column soil B with 9 gram/100 g soil of zeolite added until 12.3 pore volumes was reached; the concentration levels never got beyond 0.27 mg/l. After passing 9 pore volumes of leaching solution, the Cd concentration in the leachate reached its peak of 2.1 mg/l. For the soil A, cadmium migration was slower than that in all the other soil textures. It took more than 12 pore volumes of the leaching solution for Cd to be detected in the column effluent. The similar result was observed also in Pb (Figure 2). The result of the study can be used in determining possible applications of our natural zeolites for cadmium stabilization in soils.

Binary system

In this experiment, different amounts of zeolite were mixed with Cd and Pb-contaminated soil samples together with two pH variation. The change in Cd and Pb concentration in the leachate indicated that zeolite enhanced the sorption capacity of the soil (Figure. 3). The influence of pH was also shown, as the lower pH showed the higher sorption capacity in soil.The addition of natural zeolite strongly inhibited the leaching of cadmium and lead in all the soil samples (Figure. 3). Leachate Cd and Pb concentration of soil samples dropped when of zeolite was added to contaminated soil sample.Figure. 6 further illustrates that the result support the finding on single system, and the application of zeolite was very good for Pb and Cd contaminated soil.

The results obtained from the column an experiment of binary system was shown in Figure. 3, while Cd and Pb was not detected in the leachate from column soil until certain pore volumes was reached. After passing certain pore volumes of leaching solution, the Cd and Pb concentration in the leachate reached its peak. For the binary, lead migration was slower than lead migration that in all the other soil textures. The result of the study can be used in determining possible applications of our natural zeolites for cadmium and lead stabilization in soils.

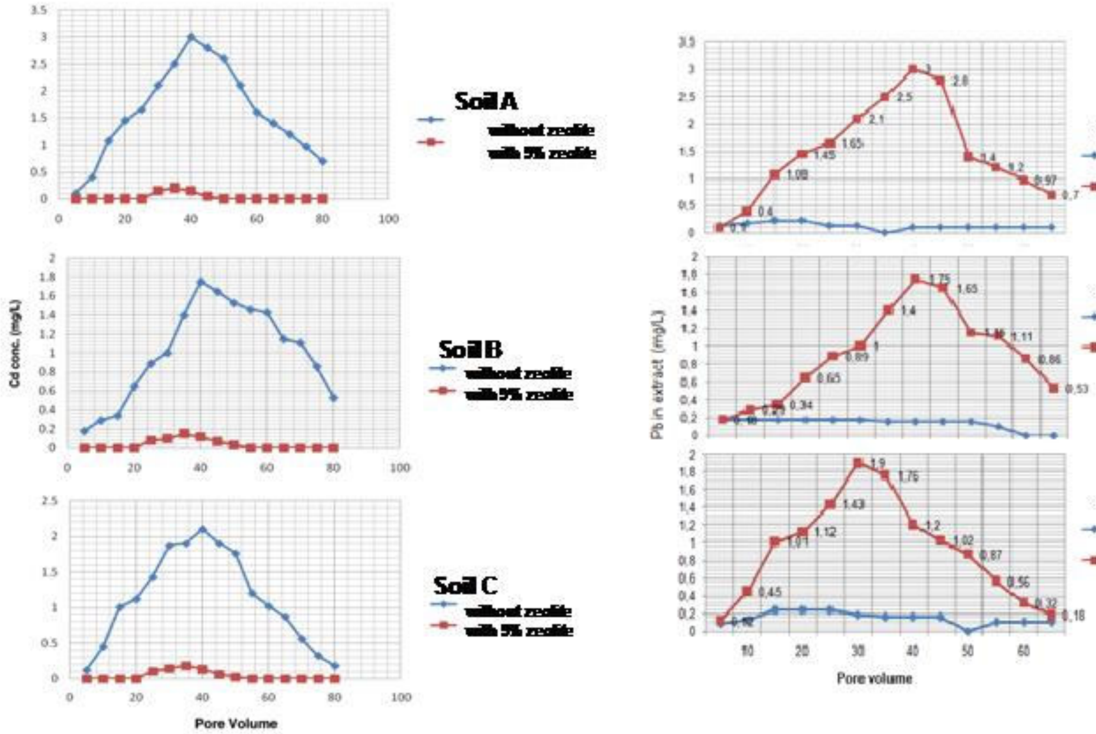

Fig. 2. Pb and Cd concentration in effluent as a function of leachate pore volume for soil A, B and C

CONCLUSION

It can be seen that the sorption generally increases with increasing pH for both Pb and Cd in single metal solution system, while increasing sorption with increasing pH is also observed in the case of binary system (see figure 1, figure 3). Compare to single system, metal sorption by our natural zeolite decrease in binary system Oh et al. (2009) reported that the sorbed quantity of Pb and Cd decreased in the bi-solute as compared to the single sorption.The latter trend for the binary system can be attributed to the fact that the aluminol and silanol groups are more protonated at low pH and hence less available to retain or adsorb the metals. However, the trend in the single metal solution system can be attributed to the interplay of proton input at low pH,which causes hydrolysis of the exchangeable silicate base of the zeolite (mostly Al in this case) on one hand and cation exchange reaction and in other words the removal of Pb and Cd from our contaminated soil on the other hand.Therefore, it can be concluded that while hydrolysis and surface adsorption reaction characterized the adsorption mechanism in the single metal system, cation exchange with functional group characterized the adsorption process in the binary metal solution system.

In soil material pH plays a major role in the sorption of heavy metals as it directly controls the solubilities of metal hydroxides (Appel and Ma, 2002) while increasing pH is said to increases cationic heavy metal retention to soil surfaces via adsorption, inner-sphere surface complexation, and/orprecipitation type reactions (McBride, 1994; Sparks, 1995; Zuhairi, 2003). However, the effects of pH on the adsorption capacity of zeolite are said to depend on the respective isoelectric points. This is due to the fact that at pH above the isoelectric point, the net negativecharge and the ionic states of active sites and hydroxyl groups do promote exchange reactions (Drever, 1988). For this study, the adsorption of Pb and Cd followed the expected trend of increasing metal uptake/removal with increasing pH especially under binary metal system(see figure 3).Thus it can be concluded that theincreasing adsorption capacity with pH underbinary system is related to the influence ofsilanol and aluminol groups that are lessprotonated with increasing pH and thus moreavailable for the adsorption of the metalions. This is also supported by the fact thatat higher pH active sites on the clay surfaceis more or less negatively charged and thus promotes cation exchange reactions. Generally, it can be concluded that natural zeolite, as a soil amendment material, is highly beneficial and suitable especially in both fine and coarse-textured soils.

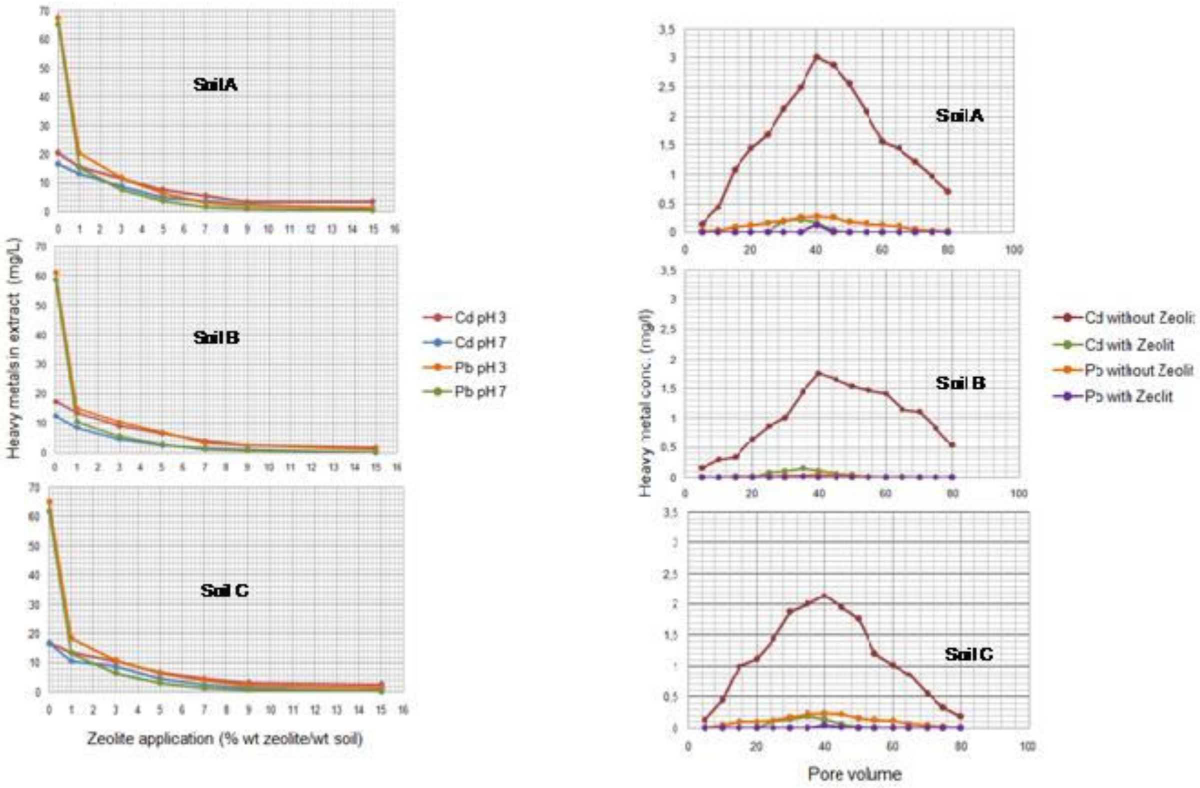

Fig.3. (a) Leachate Pb and Cd concentration from simulated contaminated soils as a function of the zeolite dosage. (b) Cd and Pb concentration in effluent as a function of leachate pore volumesimulated contaminated soils

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MOBILITY AND TOXICITY OF HEAVY METAL(LOID)S ARISING FROM CONTAMINATED WOOD ASH APPLICATION TO A PASTURE GRASSLAND SOIL

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KEYWORDS
Heavy metal toxicity, pore water, bioavailability, wood ash, arsenic, chromium

ABSTRACT

A pot experiment was conducted to investigate the fate of metal(loid)s derived from contaminated ash (≤ 10000 mg kg^{-1} As, Cr, Cu and Zn) added to an upland pasture soilthat had been prior amended with local cattle manure. Metal(loid) concentrations were measured after 9 weeks in pore water and ryegrass grown on the soil/manure-ash mixtures (0.1-3.0% vol. ash). Toxicity evaluation was performed on pore waters by means of a bacterial luminescence assay.

Both pore water and ryegrass tissue concentrations of As, Cu and Cr were elevated by ash applications compared to soils receiving no ash. Applying ash to manure amended soil buffered some phyto-toxicity effectsassociated with ash application to non-manure treated soil, by regulating pH regardless of ash application volume; this was evident from improved ryegrass biomass and bacterial luminosity concomitant to soil without ash addition. Pore water concentrations of As and Cu significantly correlated with ryegrass uptake, indicating that these elements were the most bioavailable of those investigated; Cr uptake was influenced by the volume of ash additionbut ash had no impact on either pore water or ryegrass accumulation of Zn.

The results of this study thus indicate that prior amendment of soil with manure can reduce the phyto-toxic impacts of metal(loid) contaminated ash, improve soil nutrient status and promote increased ryegrass growth.

INTRODUCTION

Waste wood ash arising from the industrial and domestic use of wood fired biomass boilers for heat production or generating electricity requires disposal or re-use. This is increasingly likely to be the case as incentives to install biomass boilers encourage the replacement of non-renewable with renewable energy sources. Wood which hasbeen treated with weatherproof protectants, paints and preservatives can contain high amounts of heavy metals and organic compounds (Balasoiu et al. 2001). After combustion of these contaminated feedstocks, and loss of more volatile organic compounds (VOC), the final ash is concentrated in both nutrients from the biomass and heavy metal(loid)s arising from the additive treatments (Balasoiu et al. 2001).

One way to dispose of wood ash is by application to land, which has a number of benefits and potential concerns associated. For example, it has been show that the addition of wood ash to soils increases pH (Bougnom et al. 2009; Klemedtsson et al. 2010 etc.) and several studies have suggested that wood ash improves crop biomass and yield (Pérez-Cruzado et al. 2010; Bougnom et al., 2012; Materechera 2012). Studies that have used wood ash generated from reclaimed waste [contaminated] feedstocks report that heavy metals derived from the ash are bioavailable and potentially phytotoxic; Lucchini et al (2013) studied the addition of a Cu rich ash (~200 g kg-1) to two agricultural soils (pH 5-6). They found that ash addition not only increased soil Cu concentrations and uptake to sunflower (*Helianthus annuus* L.), but adversely affected plant biomass yield. In that study pH increased immediately after ash addition but this was not maintained, with pH decreasing after 45 days. Jones and Quilliam (2014) experimented with similar applications of ash to a podzol soil (pH 5). The ash was produced from various ratios of contaminated and non-contaminated wood. In common with Lucchini et al (2013), the addition of Cu contaminated ash to soil increasingly resulted in raised bioavailable Cu in soil and uptake to wheat (*Triticumaestivum* L.) according to increasing proportion of contaminated wood in the feedstock. The authors conclude that 10-15% of such contaminated wood volumes being combusted with non-contaminated wood would result in an ash that could induce soil Cu concentrations exceeding statutory guidelines, if applied to land. Therefore, clearly ash derived from the combustion of wood of unknown or non-separated origin could result in even further increased heavy metal loads to soils.

The following study examines the fate of the metal(loid)s Cr, Cu, As and Zn present in excessive concentration in a wood ash generated from mixed source waste wood. A pot experiment was conducted with varying concentrations of ash in combination with farm manure, added to an upland pasture soil; concentrations of Cr, Cu, As and Zn were measured in the pore water (mobility, bioavailability) and in ryegrass (*Loliumperenne*) (plant uptake) grown in the pots. The aim was to determine the effect that application of contaminated wood ash could have on bioavailability of the metal(loids), and whether co-application with manure could mitigate phyto-toxicity and reduce the risk of the ash derived metal(loid)s leaching to waters, accumulating in soil and entering the food chain.

METHODS

Soil and amendments

Soil, manure and ash were obtained from Glensaugh experimentalresearch station and farm near Laurencekirk, Aberdeenshire(UK); 56^{o} 53’24.44” N; $2^{o}32^{'}$55.24” W A soil pit was excavated and the top 30 cm of soil bagged and returned to the laboratory (A and B horizons; organic carbon (OC) contents of ~7% and nitrogen (N) contents of ~0.6% (data not shown)). The soil was then air dried at 25^{o}Cfor 1 week before it was homogenised by hand and sieved using a 10 mm sieve. Ash was sampled from a 75kw wood fired biomass burnerwhich provides heat for the farm buildings. The feedstock for the biomass boiler consisted of mixed virgin timber and waste wood such as fencing, pallets and doors (chromated copper arsenate-CCA-treated wood). Ash was obtained directly from the boiler’s combustion chamber, bagged and returned to the laboratory. The manure, consisting ofcattle excretawas obtainedfrom the farm’s manure pit where it had partly decomposed, and dried at 25°C for easy of handling and mixing, it was then homogenised by hand. Relevant chemical characterisation of the soil, manure and ash was carried out as follows and is presented in Table 1.

Experimental pot setup

A total of 7 different treatments were tested in this experiment, with 5 replicates per treatment. To create those treatments, soil and manure (10% v:v) was first mechanically mixed using an end over end method to create a homogenous soil and manure mixture. Ash was applied to this mixture at the following volumes and mixed in the same way; 0.1%, 0.3%, 1.0% and 3.0% ash (Soil + M + A).By way of control there were pots containing only soil (Soil), soil plus manure without ash (Soil + M) and soil plus ash (Soil + A). The latter treatment was mixed according to the uppermost application volume of ash mixed with the soil and manure (3%).Treatments and controls were potted into 2 l plastic potsand left to equilibrate for 3 weeks before any further experimental work was carried out. Then, one 10 cm Rhizon sampler (EijkelkampAgrisearch equipment, Netherlands)was inserted into each pot at a 45° angle. Once the sampler was inserted into the pots 15 rye grass (*Loliumperenne*) seeds were sown in each potand soil moisture brought to75% field capacity (which was maintained throughout the experiment). Throughout the experiment pots were kept in a greenhouse with controlled temperature between 16-20°Cand natural light.

After 9 weeks pore water was extracted from each of the pots using removable plastic syringes and to determine pore water pH and for a bacterial biosensor assay.Following pore water extraction (approx. 10 weeks after the start of experimental work) rye grass was harvested by cutting 2 cm above the soil, washed using deionised water and dried at 100°C for 24h; the dry biomass weight of the grass was recorded. Ryegrass was block digested and analysed for metal(loids) by ICP-MS.

Ecotoxicity assay

Pore water samples were subject to a genetically modified luminescent bacteria *Escherichia coli* HB101 pUCD607 for toxicity (Tiensing et al. 2001). In brief, 280 µl of sample which had been pH adjusted to between 5.5-6.0 pH, was added to 96 well plates. A total of 20 µl of bacterial biosensor was added into the plates and the luminescence (relative light units; RLU) recorded after 15 minutes saturation using a Microplate Luminometer (LB 962, CentroPRO). The luminescence was calculated into the percentage luminescence compared to the soil control.

Statistical analysis

The data was analysed using one-way ANOVA with a Tukey post-hoc analysis. Prior to statistical analysis the data was tested for normality and transformed (square root or log) where necessary. The data is reported as being significantly different when $p \leq 0.05$.

RESULTS

Pore watertoxicity

Ash contained greatly elevated concentrations of As, Cr, Cu and Zn compared to soil and manure (Table 1).

Tab. 1. Metal(loid) concentrations (pseudo-total) of soil, manure and ash. Metal(loids) highlighted in bold type are those considered in the present study and all values are the mean of replicates (n=5) ± s.e.m.

mg kg^{-1}	As	Cr	Cu	Zn
Soil	4.5 ± 0.2	23.9 ± 2.1	8.8 ± 0.6	23.2 ± 1.4
Manure	5.4 ± 0.4	19.7 ± 2.1	22.6 ± 2.1	169.0 ± 11.5
Ash	9259.4 ± 649.3	9914.1 ± 714.9	8793.4 ± 632.0	4666.7 ± 373.5

The addition of ash to soil significantly increased As, Cr and Cu in pore water furthest where no manure was added. No effect on Zn was evident with or without manure (data not shown). The toxicity assay summarises the effect of the ash/manure mixtures on pore water composition; luminescence of the bacteria when exposed to the pore water collected from the soil with manure treatment was approximately 80% of luminescence of the pore water collected from the soil alone. None of the pore water collected from the soil with manure and the four concentrations of ash differed significantly from the soil and manure treatment in terms of percentage luminescence, however the pore water collected form the pots that contained soil and ash without manure had a significantly lower percentage luminescence compared to the pore water sampled from the soil and manure treatment (figure 1).

The addition of ash to the soil alone significantly increased the pH of the pore water when compared to the pore water extracted from the soil alone without ash. The pH of the soil with 3.0% ash was circumneutral.

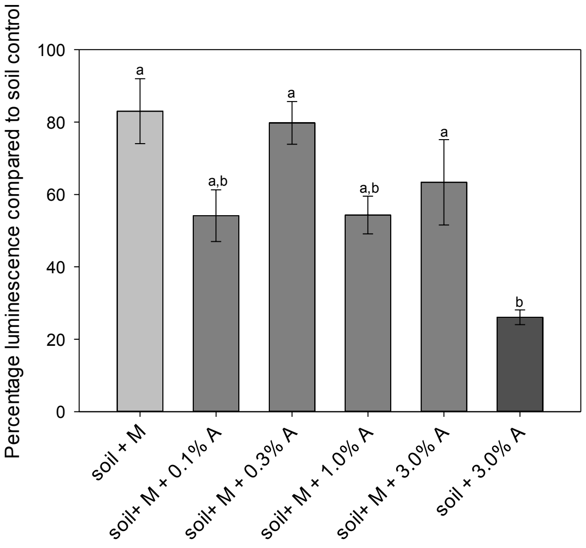

Fig. 1. Bacterial biosensor toxicity tests of pore water for the different treatments (+M = with manure; + A = with ash). Bar represent the average of the replicates and the bar is the s.e.m (n=5). Means that share the same letter are not significantly different.

Plant biomass and elemental composition

The biomass of the grass harvested from the pots which contained soil, manure and ash varied, with all having either statistically the same biomass as the soil and manure treatment or significantly greater biomass (> 10 fold). Ash added alone had no effect on biomass (data not shown).The combination of manure plus ash reduced Cu in ryegrass tissue, compared to ash added to soil alone; for As, manure addition with 1% ash resulted in greatest uptake of this metalloid to ryegrass (Figure 2). For Cr the results were mixed, whilst for Zn there was no significant effect of any treatment, in common with the trend identified in pore water concentrations (data not shown).

DISCUSSION

Combined impacts of ash and manure on As and Cr toxicity

The concentration of metal(loid)s in pore water reflects the fraction to which plants and soil animals are exposed, and has been discussed previously as a method of monitoring and risk assessment of contaminated soils (Moreno-Jimenez et al., 2011).In the present study there is a disparity between the input of As and the concentration of As in the pore water and in the plant. This unbalanced relationship between the total amount of As present in the soil and the concentration in the pore water / plant maybe explained by the effect that the amendments have on the pH of the soil. As observed in previous studies (Saarsalmi et al. 2012; Podmirseg et al. 2013) one of the greatest effects that the ash addition had on the chemical properties of the soil was to significantly raise the pH. Arsenic speciation and therefore As solubility, mobility, bioavailability and toxicity depend on a large number of factors including organic matter, redox potential, pH and phosphate concentration (Masscheleyn et al., 1991; Cao and Ma, 2004).

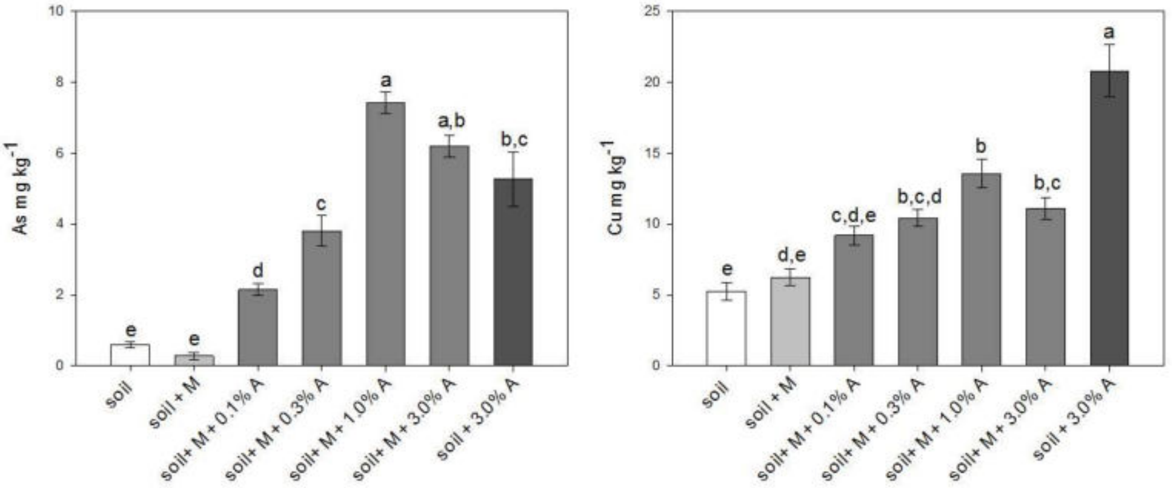

Fig. 2. Concentrations of As and Cr in the ryegrass from each of the different treatments (+M = with manure; + A = with ash). The bars represent the average of the replicates and the error bar the s.e.m (n=5). Means that share the same letter are not significantly different.

In the case of Cr, the application of ash to soil without manure caused an increase in the concentration of Cr in the pore water and plant accumulation compared to soil and ash with manure addition.The relationship between Cr in the porewater and plant is complex;in the terrestrial environment the most common forms of Cr are the trivalent (Cr(III)) and hexavalent (Cr(VI)) forms (Kimbrough et al., 1999). Cr(VI) is more toxic than Cr(III) due to its increased solubility and high oxidising potential (Pawlisz et al., 1997). It has been demonstrated that dissolved organic carbon can cause the reduction of the more toxic Cr (VI) to Cr (III) (Nakayasu et al., 1999) and that Cr (III) can then bind to the humic acid matrix (Janos et al., 2009).

Influence of soil treatments on Cu and Zn mobility and uptake

The total trace element concentration of the ash in the present study are concomitant with those previously reported in sewage sludge and exceed those reported for phosphate, nitrate fertilisers and lime (Ross, 1994). However, in contrast to As and Cr, the presence of bioavailable Cu and Zn in ash could add value to its application to soils as a means of fertilisation and fortification of plant tissues with trace metals. Despite the fact that Cu and Zn solubility increases greatly at pH < 5, the effective liming capability of ash in the present study, which increased pore water pH by ~3 units, was clearly insufficient to prevent large quantities of free Cu and Zn from ash being de-sorbed and solubilised. Several studies have reported the reduced mobility and availability of

Cu in the presence of organic amendments (reviewed in Kumpiene et al, 2008), the effects regulated by organo-metallic complexes formed between Cu and organic fractions in soil (Bernal et al, 2009). The ash used in the present study had 8800 mg kg^{-1} total Cu concentration; however, other authors have measured as high as 98450 mg kg^{-1} total Cu in ash produced from CCA treated waste wood. Needless to say such high Cu loadings added in soils would likely saturate the binding capacity of low additions of manure and promote leaching of Cu from soils. Therefore repeated additions of manure may be required to maintain stable soluble Cu concentrations and prevent Cu toxicity in plants.

CONCLUSIONS AND FURTHER WORK

There are potential environmental pollution issues associated with the application of metal(loid) contaminated wood ash to land related with leaching of contaminantsout of soil and phyto-toxicity. The particular ash used in this study had high concentrations of As, Cu, Cr and Zn, so the immediate concern is that soil metal loadings will dramatically increase with high or repeat doses of ash application. Pre-manuring soil before adding ash can buffer pH and reduce the solubility of metals in from the alkaline ash. Organic matter also provides binding sites for Cu and As; therefore phyto-toxicity can be avoided by adding manure to soils due to receive ash. The response is likely to be dose dependant.Similarly Cr loadings in soils receiving this and similarly contaminated ashes are likely to be of concern. Ash addition to soil appeared to have no consequence on the concentration of Zn both in the pore water and in the plants and, in this respect the application of Zn rich ash will only serve to raise total Zn concentrations of soil, especially if the process is repeated, with no benefits to plant nutrition. This effect may be plant species and soil specific; it remains to be seen if Zn would accumulate and re-fractionate to more soluble forms and become bioavailable. If this were the case there could be some benefits regarding fortification of crops with Zn from the ash. In general, it is unlikely that justification for repeated application of this particular ash could be gained by an increase in available Zn in any case as the risks ofAs and Cr leaching would prove too great.

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FEASIBILITY OF INTEGRATION OF AN ELECTRODIALYTIC PROCESS INTO SOIL REMEDIATION PROCEDURE FOR REMOVAL OF COPPER, CHROMIUM AND ARSENIC

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KEYWORDS
Electrodialytic treatment, pilot plant, arsenic, copper, soil suspension

INTRODUCTION

Soils polluted with heavy metals and arsenic compounds are a challenge for contaminated soil handling procedures. Traditionally, a remediation of such material involves excavation of the contaminated soil, followed by an immobilization of metal contaminants by solidification/stabilization technology prior to disposal of the material in a permitted landfill site or on-site. However those remedial actions based on solidification/stabilization technology are no longer considered a permanent solution because the pollutants are not removed from the contaminated media resulting in a need for future monitoring of a pollutants faith on site and questionable longevity of the solidified/stabilized materials (Dermont et al., 2008).

Therefore, there is a great need for a novel treatment technology that can efficiently separate heavy metals and arsenic from the soil. Among the technologies that have been in focus recently are: 1) flotation; 2) soil washing; 3) phytoremediation and 4) electrokinetic methods. All processes are affected by soil properties and speciation of the polluting compounds and process efficiency may have to be enhanced by chemicals addition, like surfactants, which were reported to improve washing and flotation (Reynier et al., 2013; Torres et al., 2012).

Another approach could be a combination of two technologies, like presented in this paper uniting soil washing and electrodialytic remediation. Application of the electrodialytic (ED) remediation developed at the Danish Technical University has been well described in last decades, but was mostly applied as laboratory and bench scale experiments with very limited mass of treated material (Ottosen & Hansen, 1992). The ED method combines the technique of electrodialysis with the electromigration of ions in the polluted soil. During the process it is possible to separate ions from soil with help of applied electric field to electrodes isolated from soil by ion-exchange membranes. Anions, like arsenite and arsenate, are removed to compartment with anode through a anion-exchange membrane and cations, of copper and chromium, are moved into a compartment with cathode through a cation-exchange membrane. Laboratory experiments proved that the ED remediation process applied on saturated soil was very effective for the removal of copper and to a certain extent chromium (Hansen et al., 1997). However As was not removed significantly in this system. This is mainly because the soil is acidified during the remediation, and in acidified soil As will mainly be present as uncharged species (H_3AsO_3 in case of As(III) and H_3AsO_4 in case of As(V)). Such uncharged species are not transported in the applied electric field. Faster remediation was showed to take place in a stirred suspension of soil than in the water saturated soil (Jensen et al., 2007; Ottosen et al., 2012). Moreover, increasing pH to pH=3-4 significantly increased arsenic species removal reaching a removal efficiency of 60% (Sun et al., 2012). It was also shown that remediation of the fine fraction of soil was faster and more energy efficient than remediation of the whole soil. Therefore if the contamination is primarily bound to the fine fraction of the soil, which is often the case, it may well be feasible to first implement soil washing to separate the less contaminated coarse fractions from the highly contaminated sludge, and then subject the fine fraction (sludge) to ED remediation, which would then be more efficient both due to the smaller mass to be treated and due to the higher efficiency of the treatment (Jensen et al., 2006). The concept was introduced earlier (Jensen et al., 2012).

This work aims to investigate the feasibility of application of the technology duet for decontamination of one of several former wood preservation plant left polluted by Cu, Cr and As (CCA) in Denmark. CCA was originally used in the impregnation process, and hot spot concentrations of copper, chromium and arsenic (1000-2000 mg - Cu/kg of soil, 300-600 mg Cr/kg and 200-1200 mg As/kg) are clearly above the Danish clean soil criteria of 500 mg Cu/kg, 500 mg Cr/kg and 20 mg As/kg. The Collstrop site only poses minimal risk to the nearby recipients and the groundwater resource in the area, but it is a standard site for wood preservation. The site is therefore used by The Capital Region of Denmark for testing remediation methods. The objective is that these methods in the future can be applied on similar sites where remediation is required due to risks towards groundwater and recipients.

METHODOLOGY

Soil sampling

Soil samples were obtained from two locations at the Collstrop contaminated site in Hillerød, Denmark. The samples differed in contamination level . Soil samples from location A were mainly used for lab scale investigations, and soil fines were obtained by wet-sieving the original soil through a 63µm sieve with water and soil from location B was excavated and washed in a soil washing facility Umweltschutz Ost GmbH in Germany. The initial concentrations are shown in Table 1. The soil samples were air dried at room temperature prior laboratory experiments, while for pilot investigations it was used as obtained from the soil washing facility.

Tab.1. Heavy metals and arsenic content in Soil samples from the two different locations

	Location A – for lab scale investigations		Location B – excavated and washed in Germany	
	Soil-A	Fine-A	Soil-B	Fine-B
Cu	1130 ±90	8500 ±1600	183 ± 80	182 ±14
Cr	300 ±20	1900 ± 200	10 ± 5	104 ±14
As	214 ±5	2080 ± 400	220 ± 80	470 ±120

Analytical procedures

Solid samples of 1.0 g of dry soil and 20.0 mL (1:1) HNO3 were heated at200 kPa (120 °C) for 30 min according to Danish Standard 259. The liquid was separated from the solid particles by vacuum through a 0.45 µm filter and diluted to 100 mL. The concentrations of metals and As in prepared liquid samples were measured with ICP (Varian 720-ES, software version: 1.1.0). Examination of the pH-dependence of metals and arsenic mobilization from soil used the following procedure: 5.0 g of dry soil and 25 mL of acid, HNO_3 in various concentrations, or basic, NaOH in various concentrations, solutions were used to make soil suspensions that were mixed for 7 days to reach equilibrium. After this time the suspensions were filtered (0.45 µm) and the filtrates were analyzed.

Electrodialytic remediation – lab and pilot scale

The electrodialytic experiments in lab scale were conducted in cylindrical cells made from polymethyl methacrylate and were built from 3 compartments; two compartments with electrolytes on sides separated by ion exchange membranes from the middle compartment, where the soil slurry was placed as shown on Figure 1. An anion exchange membrane (50 cm^2, AR204 SZRA MK III from Ionics, GE Water & Process Technologies) was placed between anode (+) and middle compartment and cation exchange membrane (50 cm^2, CR67 MK III from Ionics, GE Water & Process Technologies) was placed between catode and middle compartment. Platinated rods from Permascand were used as electrodes. Electrolytes (500 mL of 0.1 M NaNO3, pH= 2 ± 0.2 adjusted with HNO3) were circulated through the electrode compartments and the soil slurry in the middle compartment remain suspended. Application of a DC electric field to electrodes immersed in the electrolytes (compartment I and III) or directly in the treated slurry (compartment II) induces water splitting reactions that depends on polarity of electrode:

- reaction on anode (+): $2\ H2O \rightarrow O2(g) + 4H^+ + 4e^-$
- reaction on cathode (-): $2H2O + 2e- \rightarrow H_2(g)+ 2OH^-$

A placing of electrode in the slurries compartment enabled to apply current between the slurry and one electrolyte at a time, depending what kind of ions were aimed to remove. To remove cations compartments II and III were connected, where the electrode M was working as anode and the compartment I was inert in the process. Similarly connection of compartment I and II, where the electrode M was working as catode was used to remove anions from the slurry.

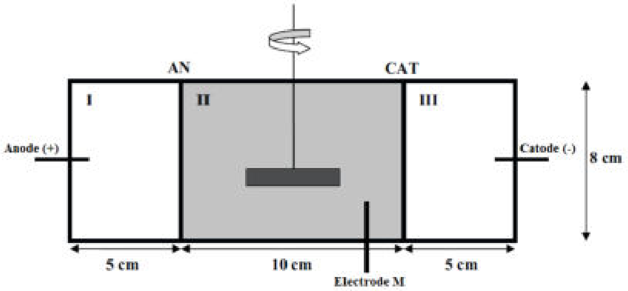

Fig.1. Principle of electrodialytic remediation of suspended soil slurry (AN – anion exchange membrane, CAT – cation exchange membrane) (Sun et al., 2012)

The experiments were performed on 35 ± 0.2 g of soil material that was suspended in 350 ± 5 mL of water, resulting in liquid to solid (L/S) ratio 10. A current of 20 ± 0.1 mA was used resulting in a current density of 0.4 mA/cm^2. After end of the experiments removal efficiency for each element was calculated as the mass of the actual heavy metal and arsenic in the electrode components (membranes, solutions in electrode compartments and on electrodes) divided by the total mass of the element found in all parts of the cell. Therefore the final results were divided into 4 groups that are defined as following:

- Anode Comp. (+) – sum of the element masses from electrolyte, anode and anion exchange membrane;
- Catode Comp. (-) – sum of the element masses from electrolyte, catode and cation exchange membrane;
- Mobilized from soil – mass of the element found in filtrate after passing 0.45 μm filter;
- Left in soil – mass of the element in dried soil after filtration with 0.45 μm filter.

The upscaled electrodialytic remediation was following the same principles as the laboratory cell, but enabled to treat 1000L of soil slurry. The compartments with ion exchange membranes where submerged in the slurry that were mixed with help of compressed air applied from the bottom of the tank, as shown on Figure 2. The upscaled plant used bigger membrane area, i.e. 2200 cm^2 each, and 25L of electrolytes were circulated. There were used different initial volumes of slurry, but the L/S ratio was the same as in the lab experiments.

The energy consumption of the ED process can be calculated by equation $E_x = \int VIdt/W$, where E is the power consumption per miligram of removed element ($Wh/mg_{removed\ x}$); V - voltage between working electrodes (V); I - current (A); t - time (h); W - the mass of the element found in the electrolytes compartment (mg). For the upscaled treatment plant power meters (SparOmeter – kWh meter from Elma Instruments) were used to measure a factual energy consumption of all electrical equipment, also for electrolytes pumps and stirring systems.

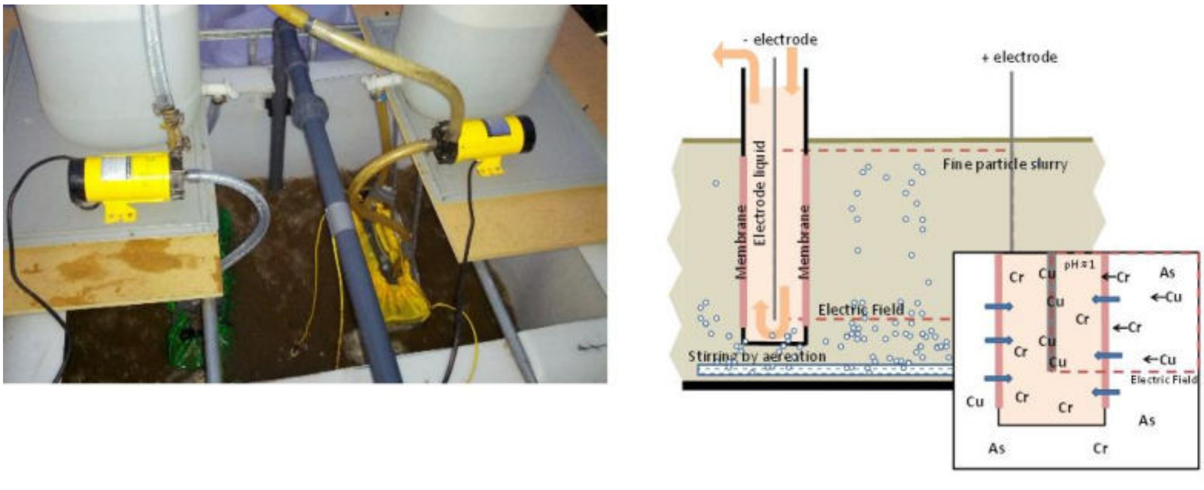

Fig. 2. Left: The prototype bench scale electrodialytic treatment with aeration system (in a bottom), electrode cassettes and an electrode liquid recycling system (green with cation exchange membranes and catholyte and yellow with anion-exchange membranes and anolyte). Right: Conceptual model of electrochemical batch. Only the setup for removal of cations, Cr and Cu, is shown. For removal of As, the electrodes and membrane are reversed.

RESULTS

Soil characteristic

The particle size distribution obtained by wet-sieving of soil A indicates that the soil consisted mostly of size fraction between <1-0.125 mm (Figure 3). However these fractions are the least contaminated by As, Cr and Cu. The highest contents of Cu, exceeding the Danish clean soil criteria of 500 mg/kg, were in sand (> 1mm) and finest fractions (<0.063 mm). All fractions surpass As the criteria that is 20 mg/kg, but the highest As content was found in the finest fractions. Chromium exceeding the clean soil criteria was found only in the finest fraction. The presence of the contaminants in coarse fractions can be a consequence of organic material occurrence, especially preserved wood particles. Though accumulation of contaminants in the finest fraction of soil brings two advantages, enable to reduce mass of treated material and increase initial contaminants content. Therefore, the washing of soil B performed on 14 tonnes of material was aiming to obtain the finest fraction that would have been used in the pilot scale investigations. The outcome of soil washing was production of 4.4 tonnes of fine fraction (Fine-B), which properties can be found in Table 1. The fine-B material was only exceeding the clean soil criteria for arsenic content, as the soil-B did not have high Cr and Cu concentration when compared to soil-A.

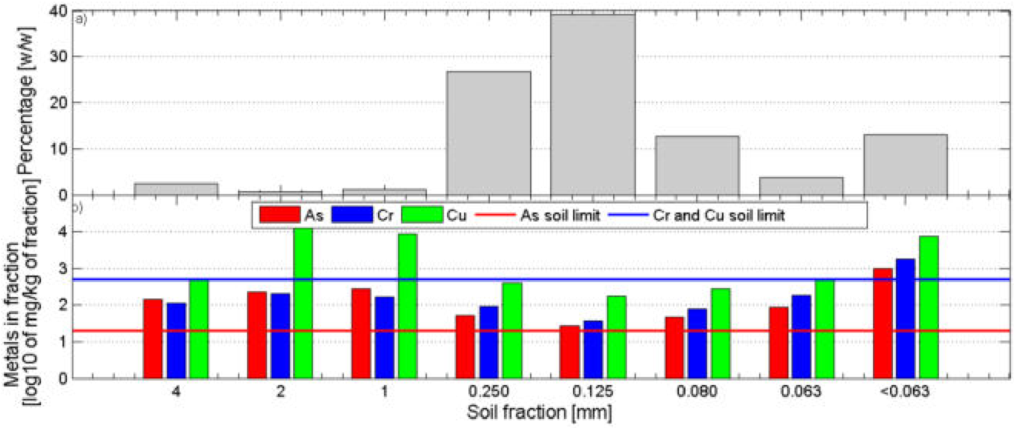

Fig. 3. Particle size distribution (a) and concentration of contaminants in each fraction size for soil sample A (As, Cr and Cu soil limits refer to Danish clean soil criteria)

The pH of slurry is a crucial parameter for electrodialytic remediation as it affects heavy metals and arsenic release. The mobilization dependence on pH is presented on Figure 4. To achieve all contaminants, i.e. As, Cr and Cu, mobilization the pH shall be decreased to below 2, where about 90% of Cu is dissolved. For mobilization of As and Cr the pH even has to be decreased to pH<1 to achieve more than 80% of mobilization. The mobilization of those compounds at low pH may be due to dissolution of contaminant bearing minerals and aluminum and iron hydroxides that are known for their adsorption capacities (co-precipitation). However the low pH conditions are limiting occurrence of arsenic anions, as its species starts to dissociate at pH above 2 (pK_{a1} of arsenate-H_3AsO_4 is 2.2 and pK_{a1} of arsenite-H_3AsO_3 is 9.3). Applying the basic conditions, especially pH above 12, reveals a different pattern for contaminants mobilization. At high pH the arsenic distinguish oneself as the most mobilized. The phenomena may be explained with desorption of As anions from amorphous iron oxide that starts at pH above 9 (Dixit and Hering, 2003).

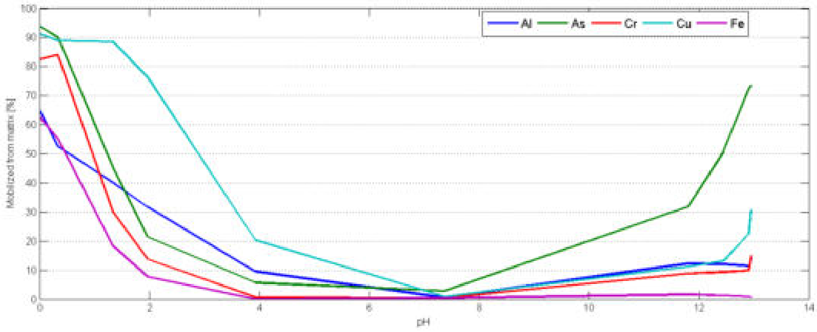

Fig. 4. Dependency of pH on metals and As mobilization from soil-A

ED- pilot and laboratory results

The evolution of main parameters in pilot electrodialytic treatment of soil-A suspension is presented on Figure 5. From a beginning of the treatment no significant Cu and As removal to the electrolytes was observed. After adding nitric acid to the soil suspension an increase in concentration of the contaminants in electrolytes could have been detected (Fig 5d). Addition of acid to the soil slurry decreased pH and resulted in metals and arsenic release to water phase enabling their removal through ion exchange membrane driven by applied current. Also addition of acid increased suspensions conductivity and as a consequence decreased voltage required to maintain applied current that results in a lower energy consumption of power supply connected to electrodes. Even though the lower arsenic mobilization occurs at higher pH this condition would be preferable to apply in electrodialytic process due to arsenic dissociation and its occurrence in anionic form. Therefore the best results for soil decontamination were obtained in laboratory experiments, when a first phase aimed to remove cations at low pH and second phase aimed to remove anions at high pH. For example a lab ED experiment on fine-A material, where during first 2days aimed to remove cations reaching pH 1.5 and 2nd phase, lasting 8 days, where anions were removed at pH 10-11 enabled to achieve 70% of Cu removal and 45% of As removal efficiency. And application of the ED lab treatment on the fine-B material, where only anions were removed at high pH enabled to remove above 70% of arsenic, which is a better results achieved in other studies, when soil fines suspension was treated in acidic conditions (Sun et al., 2012). However the soil fines quality and process conditions shall not be neglected, as they influence the ED treatment.

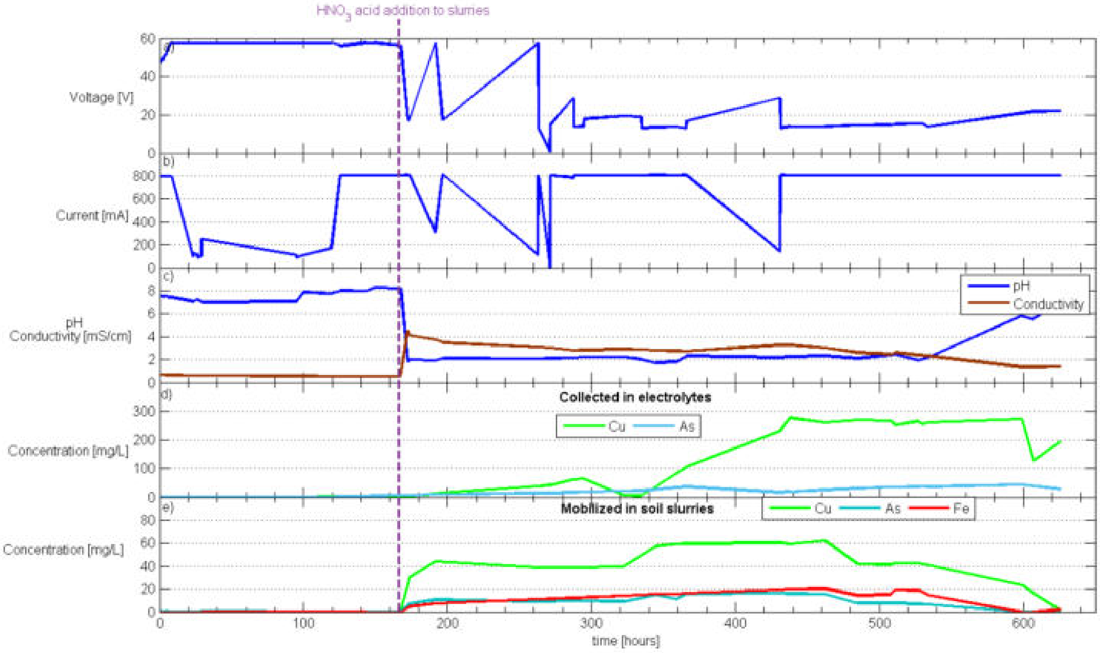

Fig. 5. Variations of main parameters during ED pilot remediation applied for soil-A suspension (45kg of soil in 515 L of water): applied voltage (a) and current (b) to electric field; pH and conductivity of suspension (c); concentration of Cu and As in electrolytes (d) and Cu, As and Fe mobilized to water phase (e)

The treatment of the fine-B material in pilot plant focused only on As removal, as only this element was exceeding the criteria. Therefore the process has been performed only at high pH conditions that can be reached in two different ways: by producing hydroxide anions with help of reaction on a cathode submerged in soil slurry or by dosing hydroxide to the slurry. Addition of NaOH increased pH immediately from 7.5 to 10.8 and resulted in some arsenic mobilization. Production of sufficient amount of $^{-}$OH on catode requires time and energy before making arsenic species available to removal. In other hand addition of other anions, especially when dosing NaOH, may have a consequence in long-term process efficiency as hydroxide and arsenic anions will compete to pass through anion exchange membrane. Comparison of processes efficiency, with regards to energy used for removal of As (Wh/mg$_{\text{removed As}}$) is presented on Figure 6. Three different pilot treatments are compared with the ED laboratory experiment on fine-material. The laboratory experiment was the most efficient with regards of energy used for ED, i.e. energy of power supply to apply current between the electrodes, which can be explained by the small size of the laboratory cell and amount of material used. The pilot treatment required 20-100 fold higher energy to remove arsenic from slurry, which indicates that electric current was not as efficiently distributed in the slurry container as it was in the laboratory cell. However the differences in power used for maintaining suspension reveals that in the laboratory experiment a low cost of energy used for ED is only a minor part of total energy spent on the treatment, as a major part of the energy was consumed by a stirring system. On the contrary the pilot setups with the fine-B material have used a very low energy for stirring, as it was applied only twice a week for period of 15 minutes, which seemed to be sufficient to keep a material in suspension to some degree. More energy was used in case of treatment of soil-A suspension, as the slurry were constantly mixed, but it has not been enough to keep a coarse fraction of soil suspended. However the energy used for ED itself is much alike for treatment acidified slurry of soil-A and basic slurry of fine-B, which can be explained by immediate arsenic mobilization and its availability for removal. As for pilot treatment of fine-B without initial pH change the process started at pH 7.5, where less As is mobilized, resulting in much lower energy efficiency for its removal. The processes are continued to reveal mechanisms of As removal and built a ground for process optimization.

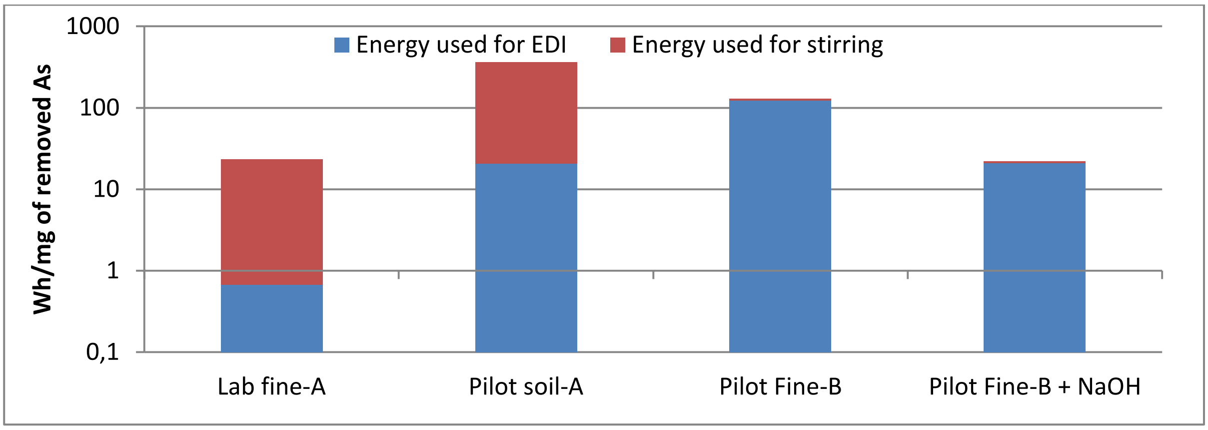

Fig. 6. Comparison of energy of the ED processes used for removal of As from soil material suspensions in laboratory cell („Lab fine-A") and in pilot runs with soil A („Pilot soil-A" - refers to energy used since suspension acidification) and fine B with NaOH addition („Pilot Fine-B+NaOH") and without any chemicals addition to the suspension („Pilot Fine-B")

CONCLUSIONS

Laboratory studies proved that it is possible to apply electrodialytic remediation for separation of arsenic, chromium and copper from soil materials. The amount of treated material can be reduced with help of soil washing that enables to separate the most contaminated soil fraction, which was found to the finest fraction.
However different approaches have to be applied to remove cations and anions, especially when scaling up the process. To remove cations it is necessary to mobilize them at low pH, bot for anions removal, especially arsenic high pH of the suspension has to be used to have sufficient arsenic mobilization and anions forms. The ED remediation was found to be feasible for up-scaling. The factors influencing the ED pilot scale, beside pH of treated suspension, is the stirring routine to maintain material suspension. The pilot plant investigations are ongoing and aim in defining the process parameters that shall be improved by proper equipment and process design.

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MECHANISMS OF INTERACTION BETWEENTRACE ELEMENTS AND MICROORGANISMS IN THE COMPLEX BIOTIC/ABIOTICSYSTEMS (BIOSORPTION AND BIOACCUMULATION)

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KEYWORDS
Molecular mechanisms, interaction, microelements, microorganisms, environment, biosorption, bioaccumulation.

ABSTRACT

The current concepts of the biosorption and bioaccumulation of microelements by microorganisms in complex biotic/abiotic systems (soils, silts, waters, etc.) were reviewed. The main factors affecting the biological absorption of microelements by prokaryotes and unicellular eukaryotes were considered. These processes largely determine the mobility and biological availability of microelements in the soil and are of great importance for the balanced mineral supply of plants.

INTRODUCTION

Microorganisms are among the important components in complex bio_mineral systems, which influence the biogeochemical cycles of microelements. The main processes of the interaction between microorganisms and microelements (Fig. 1) that have biogeochemical value are the following:

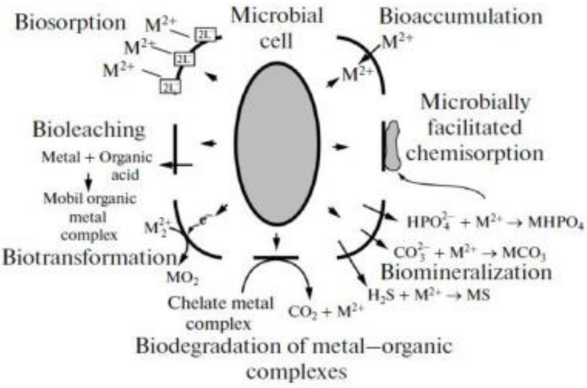

Fig. 1. Main processes of interaction of microorganisms with trace elements (Tabak et al., 2005).

1. Absorption of microelements. The absorption can occur during biosorption and bioaccumulation. Biosorption is the complex of the processes that occur on the surface of cell walls and the plasmalemma through mechanisms of ionic exchange, adsorption, complex and chelate formation, and microprecipitation (Guibal et al., 1992; Perelomov and Chulin, 2014). Biosorption does not require active membrane transport and metabolic energy consumption; the process is controlled by indirect physico-chemical reactions in solution. Bioaccumulation is the process of the biological absorption of elements by cells, followed by accumulation in the cytoplasm.
2. The transformation of microelement compounds as a result of redox processes or alkylation. The transformation can lead to the formation of products, which significantly differ from the initial compounds in the mobility and toxicity.
3. Secretion by microorganisms of organic and inorganic metabolites, which change the mobility of elements, e.g., sulfides.
4. Microorganisms are some of the main participants in the carbon cycle and therefore determine the amount and nature of organic matter in soils. Organic substances, which appear as a result of the functioning of microorganisms, can change the mobility of trace elements due to the formation of metal-organic ligand complexes in the form of chelates and intracomplex compounds or the formation of precipitates. The mobility is determined by the properties of these compounds and their concentration (Perelomov et al., 2011). In turn, the microbial degradation of metalorganic complexes also changes the composition of microelement compounds. It

should be noted that the formation of metal complexes with organic substances may in some cases decrease the decomposition of organic complexes by microorganisms and lead to the accumulation of resistant compounds. In addition to the above direct processes, microorganisms can indirectly influence the mobility of trace elements by the modification of other soil components or changing physico-chemical conditions (pH, Eh, etc.).

All of these processes should be taken into account when studying the effect of microorganisms on the forms of compounds and the mobility of microelements in complex bio-mineral systems, i.e., soils, sediments, sludge, etc. We may believe that one of the founders of the study of microbial transformation of element compound in such systems is V.I. Vernadsky. In a note submitted to the Russian Academy of Sciences in 1923 on the organization of the Biogeochemical Laboratory, he singled out specific areas of works of this laboratory, such as the role of living matter in the transformation of rocks and minerals (Vernadsky, 1923). In this paper the authors investigated the processes of sorption of trace elements by microorganisms (biosorption and bioaccumulation) and the factors that influence these processes.

BIOSORPTION

Biosorption includes several mechanisms, the most important of which are: ion exchange, adsorption and chelation. This process is often referred to bonding metals on the surface of bacterial cells (White et al., 1995). Gram-positive bacteria have a larger sorption capacity, due to the thick peptidoglycan layer of the cell walls, which contain numerous sorption positions (Beveridge, 1989). Biosorption processes are determined by two main factors, such as: 1) the surface properties of the cell membrane (charge, quantity and orientation of the metal-binding functional groups); 2) the chemical forms of the metal compounds in the liquid phase.

The titration curves of bacteria, yeasts and fungi, as well as the isolated cell walls of bacteria and bacterial polymeric compounds - mostly straight without sharp bends, which shows many different ligands (Chen et al., 1995). At least three different groups of proton-binding sites were detected on the surface of isolated cell walls of *Rhodococcus erythropolis* (Plette et al., 1995). The presence of large amounts of metal-binding sites on the surface of the cell walls has also been shown to *Pseudomonas atlantica* and *Klebsiella aerogenes* (Lion and Rochlin, 1989). Carboxyl groups are important in a bonding of metals, but the role of amino groups and phosphoryl groups are high also (Beveridge, 1981). Metals biosorption on the surface of microorganisms can take place in several stages. For *Bacillus subtilis* Beveridge and Murray (1980) suggested a two-step mechanism of interaction. At stage 1 electrostatic interaction of metal ions with functional groups on the surface of the cell membrane occurs. At the 2nd stage attached metals act as sites for further deposition of elements and initiation of the aggregates growth. A weight of such aggregates in the hydrated state can reach masses of bacterial cells (Schultze-Lam et al., 1996). These sediments are amorphous due to the high hydration initially. However, over time there is a loss of water and formation of a crystalline mineral phase.

Microorganisms produce extracellular polymeric substances (EPS). EPS composition is complex and depends on the strain of microorganisms and the conditions of their growth. Typically in the EPS polysaccharides and proteins are included and often they accompanied by the nucleic acids, lipids and humic substances (Flemming and Wingender, 2001). Such substances can be held by cells and form of capsules, or they may be separated from the cells into the environment and form a slime. EPS macromolecules contain components capable of ionization functional groups: carboxyl, phosphoryl, amino, hydroxyl, et al. The charge and nature of these functional groups are causes of selective EPS interactions with minerals, nutrients and trace elements (Chen et al., 1995). There is evidence that the non-encapsulated strains of bacteria absorb less metal than encapsulated. Because many molecules of EPS are ions, they may assist in biomineralization of metal ions and may be a potential agent for concentrating and precipitating of fine mineral particles (Scott et al., 1988).

For description of biosorption at increasing concentrations of trace elements the adsorption isotherms of the process were used. The most commonly for these purposes Langmuir and Freundlich equations were applied. Langmuir model is based on the assumption that the maximum adsorption occurs when the surface of the adsorbent presents saturated monolayer of solute molecules and the adsorption energy is constant, and that there is no migration of adsorbate molecules in the surface plane. Freundlich model based on empirical data and has been designed for heterogeneous surfaces. In addition to these models the model of Brunauer, Emmett and Teller (BET) are used sometimes. Its isotherm is a multilayer adsorption on heterogeneous sites with different binding affinity and suggests that the Langmuir isotherm describes the processes in each layer (Morley and Gadd, 1995). BET equation and Freundlich equation describes better biosorption at low concentration of the adsorbent/adsorbate. The nonideal model of competitive adsorption (NICA) is a multi-component model for competitive absorption, which takes into account the nonideal adsorbate selectivity and chemical heterogeneity of the sorbent (Plette et al., 1996). Often each of these models can be used to describe the biosorption. However, since these models were originally developed for other purposes, they should be interpreted with great caution to complex biological systems such as microorganisms. It is necessary to avoid mechanical conclusions even when there is a satisfactory description of the model.

Biosorption depends on cells age, as well as live cells or dead. For example, daily cells of *Thiothrix* (strain A1) absorbed significantly less Ni or Zn, than cells in 2-5 days of age (Shuttleworth and Unz, 1993). Biosorption capacity of dead cells can be equal, more or less than the living cells (Volesky and May-Phillips, 1995). A method of processing biomass at a preparation of dead cells is also important for the biosorption.

BIOACCUMULATION

There are two types of substances transport into a cell and from a cell - passive and active. Passive transport going to the direction of difference between electric chemical potentials, it occurs spontaneously and does not require free energy of ATP. Kinds of passive transport are simple diffusion and light diffusion. For active transport continuous supply of energy is needed (from hydrolysis of ATP, energy of electron transfer or light energy). During active transport molecules can move against an electrochemical gradient. This process consumes a significant portion of the energy of the entire cell. Absorption rate may indicate their type - bioaccumulation or biosorption. Rapid absorption that occurs within a few minutes indicates the predominance of biosorption; if the absorption of metals continues after the fast stage, it can be assumed bioaccumulation.

For absorption of essential trace elements there are specialized transport systems. However, toxic elements may also enter the cell in such manner due to the similarity of properties of the ions (the ion radius and the charge). Chromate enters the cell via transport sulfate (Cervantes and Gutierrz-Corona, 1994), and the ions of cadmium, zinc, cobalt, nickel and manganese are transported into cells *Ralstonia metallidurans (Alcaligenes eutrophus)* through the magnesium ion transport system (Nies and Silver, 1989). However, a number of trace elements requires special mechanisms and conditions for transport. Iron reducing bacteria *Geobacterial sulfurreducens* and sulfate reducing *Desulfovibrio desulfuricans* ND132 uptake Hg (II) by active transport (Schaefer et al., 2011). It has been established that the uptake of mercury by *G. sulfurreducens* strongly depends on the characteristics of binding Hg (II) thiols: some of them contributed mercury entering and methylation and other inhibited both processes. Uptake system of *D. desulfuricans* had a greater specificity than the transport system of *G. sulfurreducens* and provided methylation in the presence of strong complexing thiols (Schaefer et al., 2011).

In the transport of trace elements specific ATP-binding transporter-proteins are involved actively. They belong to the family of ABC-proteins, which are distinguished: eukaryotic ABC transporters, bacterial ABC importers and bacterial ABC exporters (Fath and Kolter, 1993). ABC-proteins are most often composed of 2 hydrophobic and 2-conservative hydrophilic ATP-binding domains fixed in the membrane. Bioaccumulation system of cells normally is regulated by physiological needs using feedback principle. However, widespread use for the transport of trace elements, especially with the little-known and unknown role of non-specific transport systems can lead to toxic effects. In this case, the mechanism intracellular sequestration is activated – binding ions by biopolymers in the cytoplasm.

FACTORS AFFECTING BIOSORPTION AND BIOACCUMULATION

Acidity. Much of the research on the effect of acidity on the sorption of trace elements by microorganisms made for biotechnologically applied concentrations - about mmol. Researches carried out for the actual concentrations of naturally occurring, much less. However, the effect of pH is directly related to the concentration used. For example, at high concentrations of lead the metal adsorption by *Atlantic pseudomonas* cells did not depend on pH (Lion and Rochlin, 1989), whereas at lower concentrations the adsorption increased with an increasing of pH. A character of pH-dependent metals absorption by microorganisms can be quite different for different ions (anions and cations) and microorganisms. Assuming similarity between the mineral and biological surfaces, it can be argued that at increase of pH occurs deprotonation of functional groups of cell membranes, which promotes the binding of cations and there is general trend of adsorption increasing with pH increasing. However, in many cases, adsorption starts again to decrease at high pH.

Presence of other ions, ionic strength and solution composition. Investigation of microelements absorption by microorganism from mixtures has particularly value due to their presence together in real environment. In such cases a competition for sorption sites is possible (Santana-Casiano et al., 1995). The ionic strength influences the element sorption by changing the activity of ions in solution, surface charge and capacity of diffuse double layer of hydrated cells. Complexation of metal cations and anions can significantly alter the sorption characteristics because absorption of complexes is often carried out by other mechanisms.

Selectivity of sorption. Some microorganisms have the ability to sorb a wide range of trace elements, while others specifically adsorb only certain elements.

RedOx conditions. Redox reactions, as is known, are composed of two half-reactions, each involving an electron acceptor (oxidizing agent) and an electron donor (reducing agent), i.e., the oxidized and reduced forms of one compound (element), which are called the conjugate pair or redox pair. The oxidized forms of U, Pd, Se, Tc, Mo, Cr, and others are well dissolved in aqueous media and more mobile in aerobic groundwater compared with reduced forms of these elements (Perelomov and Chulin, 2014). The oxidized forms of trace elements in solution are represented mainly by anions; therefore, they are usually weakly sorbed on negatively charged surfaces, which are widely distributed in nature. Reduction leads in general to the formation of sedentary precipitation (oxides, hydroxides, etc.).

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PHYTOREMEDIATION TECHNOLOGY FOR CONTAMINATED SITES IN KHARKIV REGION, EAST UKRAINE

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KEYWORDS
Constructed wetlands, phytoremediation, wastewaters, Ukraine, rural.

ABSTRACT

Since 90th of the last centuryphytotechnology is widely applied in East Ukraine for remediation of wastewaters, sludge and soil. The most popular technology in Kharkiv region (c.a. 3000000 inhabitants) is constructed wetlands (CW). CW are engineered ecosystems which act as biofilters to eliminate variety contaminants from wastewater. Energy output from CWs is ~237% of the input for biofuel production.Most of CW in Kharkiv region operate in small settlements situated far from sewage grid, have a limited financial resources and energy supply problems together with a lack of qualified staff. Our assessment of 37 CW revealed that the removal efficiency of contaminants from wastewater and sludge strongly depended on the size of surface area of reed beds, vegetation cover, operational control, inputs quality, retention time and less depended on seasons to make it efficient operation during contrast climate conditions. The military actions in East Ukraine and its strong influence not only on social and economic, but also on environmental conditions, leads to the contamination of soil, water and air by chemicals, mainly titanium, vanadium, lead, cadmium and sulfates. Taking into account these challenges for East Ukraine, new phytoremediation technology could be applied for the soil and other contaminated sites remediation. In addition, the proposed technology will be introduced for remediation of former mining sites are located in Central Slovakia.

INTRODUCTION

Since the end of the last century phytotechnology is widely applied in East Ukraine for remediation of wastewaters, sludge and soil. The most popular technology in Kharkiv region (c.a. 3000000 inhabitants) is constructed wetlands (CW).CWs are engineered ecosystems which act as biofilters to eliminate nutrients, pathogenic microorganisms, persistent organic pollutants, xenobiotics and trace elementsfrom industrial and domestic wastewater streams within a semi-controlled environment (Kadlec and Knight, 1996).

Different processes (sorption, co-precipitation, absorption, nitrification-denitrification and deposition) lead to compounds accumulation in the wetland substrate and its removal. The CW efficiency depends on inlet contaminants concentrations, hydraulic loading, pH, redox conditions, temperature, presence/absence of the consortium plants/bacteria, species variability and anthropogenic factors (Kadlec and Wallace, 2009). Constructed wetlands generally show high efficiency in removal of suspended solids, BOD_5 and COD whereas removal efficiency regarding nutrients (N and P) is lower and more variable (Garcia et al., 2010).Moreover,the net life-cycle energy output of CW can be used for biofuel production and enhanced through optimizing the nitrogen supply, hydrologic flow patterns and plant species selection (Liu et al., 2013).

Since the 1960s, CWs have been developing in different countries simultaneously and various synonymous names are used to indicate the same class of objects: “man-made wetlands”, “artificial wetlands”, “reed beds”, “engineered wetlands” and “bioplato”. The last name of CWs is mainly used in Ukraine and Russia (Stolberg, 2002).

In Ukraine CWs have been first developed and applied for purification of polluted surface waters in lakes, rivers and canals yet in 1980s. The first CW (“bioplato”) facilities for domestic wastewater treatment have been designed and constructed in 1998 at the VelykiProkhody village near the city of Kharkiv (Stolberg, 2002). During the last decade the number of CWs in Ukraine has increased to somewhat 50 operation sites as these are considered an efficient alternative to conventional wastewater treatment systems, cost-effective and environmentally friendly bio-processes for purification of contaminated waters. Most of CWs in Ukraine are operated in small rural settlements which are located far away from the central sewage grid, have limited financial resources and energy supply shortages together with a lack of qualified staff for the maintaining and operating more sophisticated treatment systems.

This work aimed at assessing the performance of CWs in Kharkiv region, Ukraine by (i) monitoring common physico-chemical parameters (pH, BOD_5, COD, suspended solids (SS), surfactants, orthophosphates and total nitrogen) of wastewaters effluents and influents on operated CWs in rural areas; (ii) evaluating the operating conditions of the CWs and their efficiency to treat domestic wastewaters and (iii) comparing their treatment efficiency to the conventional wastewater treatment facilities.

MATERIALS AND METHODS

The Kharkiv region (East Ukraine) is one of the most industrialised and urbanised areas of Ukraine. In spite of the high population and industries density (87 person/km^2), the region suffers from the shortage of available water resources (Vystavna et al., 2012). The climate of the study area is a typical for the Forest-Steppe natural zone i.e. moderate with distinct four seasons. The principle water contamination sources are run-off from urban and agricultural areas, untreated wastewaters from small communities, agriculture and industries located on the rural area (Vystavna et al., 2013).

In the framework of the Kharkiv Municipal Environmental Program (2013, 2014 and 2015) 37 CWs were assessed in the Kharkiv region (c.a. 3,000,000 inhabitants, 31415 km^2 of the area). As the preliminary results, 80% of CWs were in the non-operating conditions due to the reduction of wastewaters, absence of the funding for the maintenance and lack of the vegetation. Therefore, the paper presented the results on the detailed assessment of the nine so called ‘bioplato’ hybrid CWs (Figure 1) were studied in Kharkiv region, East Ukraine.

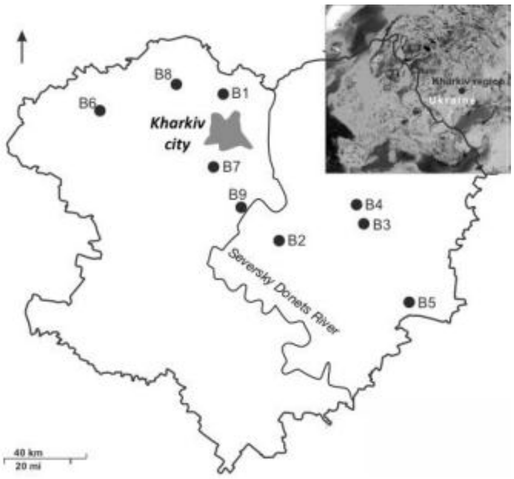

Fig. 1. The location of the studied “bioplato” CWs (B1 – B9) in Kharkiv region, East Ukraine

Studied wetlands were located in the different parts of the region and were designed in the same way (Figure 2) to treat domestic wastewaters from small towns and rural settlements (B1, B3, B4, B6 and B9), effluents from hospitals (B7 and B8), prison (B2) and orphan house (B5).

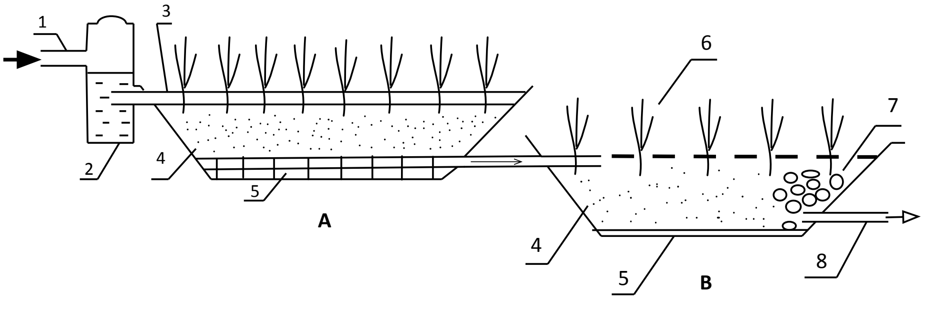

Fig. 2. Typical design of the “bioplato” CWs (*A* – a vertical flow unit and *B* – a horizontal subsurface flow unit): 1 – influent; 2 - sedimentation tank; 3 – clarified wastewater; 4 – filtering substrate; 5 – drainage pipes; 6 – macrophytes; 7 – drainage and 8 – effluent.

Wastewater samples were taken at each site from inlet and outlet points during the period of October 2012, 2013 and 2014. Samples were taken using the polyethylene bottles (2 L) for the analysis of pH, hardness, mineralization, suspended solids (SS), COD, BOD_5, anionic surface active agents (surfactants), orthophosphates (PO_4^{3-}), ammonium (NH^+_4), nitrites (NO^-_2), nitrates (NO^-_3), and glass bottles (0.5 L) for the detection of dissolved oxygen (DO).

The removal efficiency of contaminants on studied CWs was estimated as the percent reduction that refers to the decrease of the concentration between the inlet and outlet using the following formula:

$$\Delta C_i\ (\%)=(1 - C_i^{out}/\ C_i^{in}) \times 100\% \qquad (Eq.1)$$

ΔC_i, % - percent reduction of$i$ – parameter; C_i^{out}*and* $C_i^{in}$are the inlet and outlet concentrations in $mg\mathrm{L}^{-1}$ of i - parameter.

According to the removal efficiency (RE) the studied CWs were then ranked as: low (L) efficiency facilities (RE less than 50%); medium (M) efficiency facilities (RE from 50 to 80 %), and high (H) efficiency facilities (RE more than 80%).

RESULTS AND DISCUSSIONS

Taking into account that all studied CWs had the same construction type, were located in quite similar environmental conditions (temperature, solar radiation, humidity), were planted with the same macrophyte species, we assumed that differences in the removal efficiency may be attributed to differences in inflow concentrations, construction work quality and operational conditions.

All studied CWs were designed to treat domestic type of wastewaters with high contents of organic pollutants. Results of our study demonstrate that CWs can effectively reduce the output of COD and BOD_5 with the removal efficiency at 80% or above for the most of cases and the data was close to these on the traditional wastewater treatment efficiency (Figure 3).

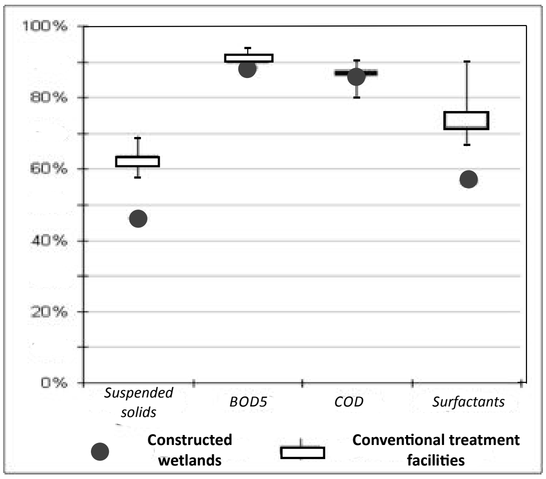

Fig. 3. The calculated treatment efficiency of studied CWs and conventional treatment facilities

The removal of SS was lower than measured at conventional treatment facilities, mostly because of the reconstruction of the settling tanks. Higher removal was found at some sites (B2 and B9), where a large patch of natural wetland was included into treatment chain thus facilitating the complexation and sedimentation of organic matter.

Nitrogen removal efficiency was variable and lower if compared to the removal of SS, BOD_5 and COD, but it was in the agreement with data reported from different cases (Rousseau et al., 2004; Garcia et al., 2010; Vymazal, 2011). In CWs, ammonium is removed by volatilization, adsorption, plant uptake and nitrification. High nitrogen removal (more than 80%) was detected at sites (B2 and B9) with the largest area (11000 m^2) and intensive covering by natural vegetation (more than 80% of the reed bed) that likely stimulated the nitrogen uptake by plants. The low removal efficiency of other CWs can be explained by relatively small area of the reed beds (760 m^2 and 1550 m^2 respectively) (Table 1) and high input concentration of total nitrogen that was not eliminated by plants uptake.

Orthophosphates removal in CWs takes place by plant uptake, accretion of wetland soil, microbial immobilization, retention by root media and precipitation in water column (Vymazal, 2011). B1, B5, B6, B7 and B8 showed low orthophosphates removal efficiency (less than 50%). Among them B1 and B7 showed the lowest removal efficiency of orthophosphates, possibly, due to the small area of reed beds (Table 1) that was not sufficient foreffective biological treatment. Additionally B1 had the high inflow concentration of total nitrogen and orthophosphates. The reasons of high inflow concentrations of total nitrogen and orthophosphate were explained by discharge from the local small cheese factory to the CW, which was not initially designed for such type of wastewaters.

Surfactants were removed at the efficiency is less than 50% at most of CWs.

Tab. 1. Parameters of the studied 'bioplato' CWs in Kharkiv region, East Ukraine

Constructed wetland locations	Year of construction	Total treatment area, m^2	Mean wastewater discharge, m^3 d^{-1} actual/designed	Water residence time, d	Dominating macrophyte species	Calculated treatment efficiency,%						Efficiency type
						SS	BOD	COD	N total	Surfactants	Orthophosph.	
B1 village	1998	760	10/40	15	*Phragmites australis (Cav.) Trin. ex Steud., Scirpussylvaticus L., Typha latifolia L.*	*56*	*88*	*85*	*45*	*31*	*10*	*L*
B2 prison	2004	11000	700/700	11	*Phragmites australis (Cav.) Trin. ex Steud.*	*99*	*95*	*90*	*81*	*91*	*56*	*H*
B3 village	2004	4500	15/70	15	*Typha latifolia L., Typha angustifolia L., Phragmites australis (Cav.) Trin. ex Steud.*	*81*	*88*	*87*	*24*	*50*	*96*	*M*
B4 town	2011	9385	400/400	11	*Phragmites australis (Cav.) Trin. ex Steud., Typha latifolia L., Scirpussylvaticus L*	*82*	*90*	*86*	*45*	*44*	*66*	*M*
B5 village	2007	2800	60/100	14	*Phragmites australis (Cav.) Trin. ex Steud., Typha latifolia L., Scirpussylvaticus L*	*89*	*90*	*80*	*45*	*61*	*75*	*M*
B6 village	2010	3400	80/130	13	*Phragmites australis (Cav.) Trin. ex Steud., Scirpussylvaticus L., Typha latifolia L.*	*74*	*74*	*76*	*56*	*42*	*66*	*M*
B7 village	2011	2750	70/100	13	*Phragmites australis (Cav.) Trin. ex Steud., Scirpussylvaticus L., Typha latifolia L.*	*41*	*88*	*80*	*15*	*48*	*20*	*L*
B8 town, hospital	2003	1550	20/100	14	*Phragmites australis (Cav.) Trin. ex Steud., Scirpussylvaticus L., Typha latifolia L.*	*21*	*67*	*60*	*60*	*87*	*40*	*L*
B9 town, Paper Mill	2012	1650	10/80	15	*Phragmites australis (Cav.) Trin. ex Steud., Scirpussylvaticus L., Typha latifolia L.*	*95*	*94*	*90*	*81*	*87*	*91*	*H*

The reduction in removal capabilities of CWs is often related to functioning and/or maturation issues (clogging, shading, matrix, saturation, decrease in retention time, appearance of preferential hydraulic pathways, etc.) and the system enhancement and continuous control could increase the removal efficiency of CWs.

At the same time, the conventional and CW treatment facilities have comparable removal efficiency of BOD_5, COD, SS and surfactants. The adjustment of CWs as an ecological engineering system during treatment, i.e. providing for longer residence time, relevant operational conditions, control of inflow concentration, as well as an established microbial community and vegetation might improve the overall efficiency of CWs.

PERSPECTIVES

The military actions in East Ukraine and its strong influence not only on social and economic, but also on environmental conditions, leads to the contamination of soil, water and air by chemicals, mainly titanium, vanadium, lead, cadmium and sulfates. Taking into account these challenges for East Ukraine, new phytoremediation technology could be applied for the soil and other contaminated sites remediation. In addition, the proposed technology will be introduced for remediation of former mining sites are located in Central Slovakia.

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NEW PHYTOTECHNOLOGY FOR CLEANING CONTAMINATED MILITARY SITES IN SLOVAKIA AND UKRAINE

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KEYWORDS

military contaminated soils; *miscanthus x giganteus*; heavy metals; uptaken peculiarities, biomass production

ABSTRACT

Optimal use of land for food, energy, materials, and phytoremediation of degraded lands are both prominent sustainability issues. *Miscanthus x gignateus*, a C-4 perennial grass, has a high biomass productivity accompanied by good water use efficiency and low nutrient demands. Plant grows well on slightly contaminated and marginal lands that are not being used for agricultural purpose including food crops production. *Miscanthus x giganteus* has the potential to improve soil quality by adding organic matter to soil, while as a perennial grass, it has advantages to reduce water and wind erosion. Plant can be harvested and used in place for combustion heating including in a pelleted form, or potentially be exported to be processed for liquid biofuels. Long-term observation research includes testing the productivity of *miscanthus x gigantheus* on the contaminated soils at thepost-military sites, including those at Sliac, Slovakia and Kamenetz-Podilsky, Ukraine. The main goal of the research is to explore the effect of the plant on soil quality and contaminant fate. Pot studies have shown that plant grows well on soils from appointed contaminated post-military sites; there is a slow uptaken of heavy metals to the above surface parts of the plant. Rates and extent of contaminant uptake are critical factors in considering whether to use the biomass as alternative energy source.

INTRODUCTION

Phytotechnology is currently becoming a proven technique (Davis et al, 2003;Suresh and Ravishankar, 2004; Kulakow and Pidlisnyuk, 2010; Pidlisnyuk et al., 2014a). The method is inexpensive and ecologically friendly, effective for large areas with small and medium concentrations of contaminants and has a big potential for cleaning brownfields and contaminated sites (Witters et al, 2012).

In accordance with the European Commission assessment report (EEA 2007) there are 250.000 contaminated sites within the EU which require urgent attention, and in the US the number of Superfund sites is estimated as 1289 in 2011 in accordance with the National Priorities List (EPA 2013). In Slovakia large brownfields are at the former mining production sites, and relatively less contaminated sites are widely speaded at the agricultural regions which have smaller sizes (Kobza 2005; Report of SME 2009). In Ukraine the intensively and medium contaminated places are located mainly at the mining territories, and biggest numbers are reported for industrially developed East (Report of MENP 2012).

Using conventional remediation technologies such as excavation and land filling, physico-chemical treatment (washing), biological treatment and thermal desorption, estimated expenses are up to 129 \$ /m^3 in Europe and up to 252 \$ /m^3 in the US (Witters et al, 2012). That approach can be preferentially used for strongly contaminated sites. Current waste management strategy underlines that not all toxic substances have to be removed, but only those which have a high potential impact to human health and /or environment not only while in soil, but also after remediation (Van-Camp et al, 2004).

Remediation activities should be in line with sustainable development approaches (Haemers 2009) and sustainable management of contaminated land has two main pillars: selection of the most appropriate technology and using sustainability principles (Vegter 2001; Pidlisnyuk et al, 2013). This is formulated in guideline documents for implementation of green remediation technologies (Rock 2003; EPA 2010; Pidlisnyuk and Stefanovska, 2014).

METHODS AND METHODOLOGY

A growing number of research investigations are focused on the union of two general processes: phytoremediation and production of biofuel crops (Witters et al, 2009; Los et al, 2011; Hromadko et al, 2010;

Nesvetov 2010; Pidlisnyuk 2012). There are a number of reasons (Witters et al, 2009), but the main ones are connected with increasing demand for biomass production as alternative energy sources (Rosillo-Calle et al, 2006) and possibility to restore marginal land to agricultural food crop use (Davis et al, 2014; Stefanovska et al, 2015). Second generation biofuel crops include short rotation trees and annual or perennial grasses; among perennial grasses *miscanthus x giganteus* is considered as the most promising (Pidlisnyuk 2012). This crop is native from Southern Asia, has a good adaptive potential in European Union countries and USA, has high harvest yields and may be grown in the relatively poor soils (Techer et al,2012; Pidlisnyuk et al, 2014b).

Miscanthus was already introduced in Slovakia, Ukraine and USA and exhibited good production properties Nesterov 2010; Stefanovska et al, 2011; Pidlisnyuk et al, 2014b; Davis et al, 2014; Stefanovska et al, 2015). Long-terminvestigation converning using *miscathus x giganteus* for restouration of post-military sites has been initiated in Slovakia and Ukraine. In Slovakia the research site is at the former SU air-force airport in Sliac,Central Slovakia and in Ukraine the research site is at the former military storage in Kamenetz-Podilsky, Western Ukraine.

Pot experiment was used when plants have been grown at the contaminated soils from the selected sites. The soils sampling were done in accordance with the standard approach presented at GOST,1984.

The coordination of places were soils samplings were taken out was the following ones:

in Slovakia: $48^{0}38^{'}38.6^{''}$N $19^{0}08^{'}25.9^{''}$E; in Ukraine:Latitude – 48,680910; Longitude – 26,58025.

In each of the pots the contaminated soil was mixed with the relatively clean soils from the territory located near the appointed research places, and different combinations of mixtering were applied. There were 14 kg of mixtured soil in each of the pots in Slovakia and 7 kg of mixtured soils in Ukraine; and two experiments were going on in parallel. For experiment in Slovakia the vegetation season in 2014 started on April, 30th and finished on December,10th; for Ukraine the vegetation season in 2014started on June, 6th and finished on November, 19th.

The analysis of heavy metals content in the soil, and plants' parts: roots, stems and leaves was provided by Rentgen-fluorescent analysis using analizator Expert-3L, produced in Ukraine. The preparation of soil and plant samples to the analysis was done in accordance with ISO 11464-2001 and three parallel measurements of each testing example was done.

RESULTS AND DISCUSSIONS

In 2014 the long-term observation research on growing *miscathus x giganteus*at the contaminated soils from post military sites has been initiated in Slovakia and Ukraine. Pictures 1 and 2 illustrated the *miscanthusxgiganteus* growing in pots with mixtured contaminated soils, consequently, taken from Sliac and Kamenetz-Podilsky.

The monitoring of uptaken heavy metals: Cr,Mn,Zn,Pb as well as As to the *miscanthusxgigantheus* leaves was provided along all vegetation season, and overall uptaken of the same heavy metals to the roots, stems, leaves of *miscathus x giganteus* was determined at the end of the vegetation season.

Laboratory pot experiment confirmed the ability of *miscathus x giganteus* to grow at the contaminated soils. Results shown that there is only slight correlation between increasing concentrations of contaminants at the diluted soil and their up taken to the above part of the plants. That results confirmed the similar research published recently (Kocon and Matyka, 2012). More over, the main part of heavy metals was uptaken to the leaves at the beginning of the vegetation season (mainly during first two month) and remains relatively stable till the end of vegetation season. The uptaken amount of heavy metals was not essential by above surface plants and preliminary was under the limited levels. The heavy metals were in the following line in terms of moving from the contaminated mixture soils to the plant: Fe>Cu>Mn, and only a very limited amount of Cr and Zn wes detected at the plants' parts. That regularities were observed for both mixtured soils from the research sites in Slovakia and Ukraine. The obtained research shown that utilization of the biomass obtained as an energy resource is attractive and can even turn phytoremediation into a profit making operation.

The 2015th long term researchis focused at the monitoring of the phytoprocess during second year of *miscanthusxgigantheus* growing at the contaminated soils from post-military sites in Slovakia and Ukraine.

The further practical use of research plant for energy production and phytoremediation of contaminated sites in Slovakia and Ukraine looks promising taking into account cost&benefit analysis and real chances to be accepted compare with expensive conventional remediation during period of low financial support for remediation measures.

Fig. 1. Growing *miscanthus x giganteus* at the post-military contaminated mixtured soils from Sliac,Slovakia as for August 12th,2014

Fig. 2. Growing *miscanthus x giganteus* at the post-military contaminated mixtured soils from Kamenetz-Podilsky,Ukraine as for July,5th,2014.

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THERMAL DESORPTION TECHNOLOGY: FROM LABORATORY TO FULL-SCALE APPLICATION

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KEYWORDS
Thermal desorption, petroleum hydrocarbons, pesticides

ABSTRACT

Thermal desorption is a fast and effective remediation technology. Technology can be operated in various configurations which can differ in the way of heating, working pressure, gaseous stream processing etc. DEKONTA own four types of desorption units that can be used for laboratory or pilot scale trials. First is a laboratory retort with a working temperature up to 550 °C and sample volume up to 50 mL. Second is a vacuum semi-pilot scale unit with indirect heating system. Maximum jacket temperature of this unit is 400 °C, volume of the mixed chamber is 100 L and the lowest absolute pressure in the chamber is 50 mbar. Besides the vacuum indirectly heated unit a unit with similar parameters but with direct microwave heating is also available for testing. Fourth unit is an indirectly heated continuous unit with operating temperature up to 500 °C and a capacity of 1-2 tons per hour. This unit was designed based on results achieved with indirectly heated semi-pilot unit. All four units are used for research purposes and also for verifying the effectiveness and suitability of the thermal desorption method for certain contaminated matrix. Trials are not focused only on the efficiency but also the off-gas quality or the material behavior, such as its tendency to coking, lumping etc. are important parameters for the process design.

LABORATORY AND SEMI-PILOT TRIALS

Thermal desorption is a very effective and fast remediation technology which can be used for treatment of various types of contamination – petroleum hydrocarbons, PCBs, pesticides, mercury etc. It removes contaminants from soil, sludge or sediment by heating the input material in "thermal desorber" to evaporate the contaminants. Evaporation changes the contaminants into vapors (gases) and separates them from the solid material. The final temperatures vary from relatively low temperatures up to 600 °C.
Through years DEKONTA procured and developed several units which can be used for laboratory, semi-pilot and pilot testing. More than 250 trials have been already carried out.

Laboratory desorption tests represent a first step for desorption process design. Laboratory trials can prove if this method is usable or not which is if it is possible to reach desired efficiency. It can also give information about condensate type and its distribution via temperature range.
Laboratory tests are useful – first information is always needed but cannot give enough information about process itself. Besides efficiency other parameters can be crucial for the process and those parameters cannot be observed during laboratory tests, e.g. off-gas quality, tendency to lumping, coking, dustiness etc. Moreover laboratory tests are burdened with relatively high aberrance which caused by small amount of the input sample.

Semi-pilot scale trials help to see more details in the input material processing. The amount of released gas is much bigger so even minor portions can be detected e.g. sulfur oxides, nitrogen oxides, methane, hydrogen, heavy metals etc. Those minor fractions of the off-gas may be important in the design of full-scale process because they can be source of extra costs for off-gas treatment. Dustiness, i.e. high content of very fine particles may cause filter dusting or dust could get through the filter and can clog the filter or the system for off-gas treatment. Lumping is source of energy loss – it creates barrier which slows down the heat transfer to bulk of processed material. It can even cause pasting of feeder and discharger.

Testing retort description

Thermal desorption retort kit (Fig. 1) is placed in steel case which enables easy handling and operation. It consists of retort, cooling lid and cylinder for condensate collection.

Fig. 1. Testing retort – (1) retort chamber, (2) condenser, (3) cylinder for condensate.

Testing vacuum dryer description

Semi-pilot unit is vacuum indirectly heated system which consists of a mixed dryer, condensation unit and thermal unit. Unit parameters are:

- volume: 100 L
- mixer speed: 0 – 100 rpm
- max. jacket temperature 400 °C
- operating pressure: 20 – 800 mbar

Unit can be connect to PC and display process data as jacket temperature, product temperature, pressure, mixer speed and energy consumption of the mixer. Condensation unit has its own manometer so the pressure drop over the dust filter or over the condenser can be checked.

Unit can be modified for continuous gas sampling and also for continuous inertization of the system if necessary. Inert gas can be brought into the dryer and/or into the condensation unit. Off-gas can be sampled from condensation unit.

Fig. 2. Mixed dryer of semi-pilot testing unit.

Fig. 3. Condensation unit of semi-pilot testing unit.

RESULTS

As examples three types of tests were chosen – filter cake from refinery, oil sludge and rubble contaminated by pesticides. For all three matrices laboratory and semi-pilot trials were carried out.

Tab. 1. Overview and summary of selected tests.

Material	Contamination	Concentration	Type of process	Efficiency
Filter cake	petroleum hydrocarbons	297 000 mg/kg NEL	laboratory test	65 %
			semi-pilot test	76 %
Oil sludge	petroleum hydrocarbons	220 000 mg/kg NEL	laboratory test	88 %
			semi-pilot test	94 %
Rubble	pesticides (HCH)	240 mg/kg HCH	laboratory test	95 %
			semi-pilot test	99 %

First material was quite easy to handle. It can be described as very fine clay with high content of oil. Laboratory test showed poor efficiency at temperature 400°C and no sign of sintering. Semi-pilot tests showed that the highest portion of the oil comes out at temperature 350 °C at 200 mbar. Methane presence was observed.

Oil sludge is more complicated material. Laboratory trials showed good efficiency, sintering was observed. Semi-pilot tests also showed very good efficiency but inertization was needed since there was relatively high concentration of methane, carbon monoxide and at higher temperatures even hydrogen. Other problems were observed during condensation - part of higher hydrocarbons was evaporated with water vapor which caused condenser blocking and during trial incondensable oily aerosol developed. Laboratory trials showed that there is a risk of sintering and lumping. That was confirmed. Thick hard layer of dryer material was formed and blocked the feeding and discharge openings.

Rubble was the easiest to handle. During both, laboratory and semi-pilot scale there were problems with condensation of pesticides which crystalized in condensation system. This can be handled by different type of condensation system.

Laboratory and semi-pilot tests helped to know the behaviour and properties of the processed samples. Rubble can be tested with use of pilot unit while oil sludge is not treatable with use of pilot unit. Whole system would need some modification. Filter cake is treatable with use of pilot unit but the efficiency of the process is not certain. Rotary kiln could be use undoubtadly if there would be a demand for oil recycling. Maximal reachable efficiency must be verified by pilot tests.

PILOT SCALE PLANT DESIGN AND TESTING

Based on results of the project no. FR-TI1/059 the continuous plant was designed and constructed. Aim of the project no. FR-TI1/059 was to connect catalytic incinerator directly to thermal desorption unit. Testing semi-pilot unit was used in this project.

Size of unit was determined by demand of mobility. It is devised as modular system which constists of:

- rotary kiln (Fig. 4)
- off-gas pretreatment (Fig. 5)
- supply unit 1
- supply unit 2 – control room.

Fig. 4. Rotary kiln of continuous thermal desorption pilot unit.

Fig. 5. Off-gas pretreatment module of continuous thermal desorption pilot unit.

Pilot plant unit has these parameters:

- capacity: 1 – 2 tons per hour
- diameter: 1,2 m, lenght: 8 m
- rotation: 0 – 10 rpm
- indirect heating system
- temperature: 400 – 500 °C

Rotary kiln continuously process 1 – 2 tons of input material per hour. Off-gas is dusted off by cyclone and fine filter. If needed, off-gas can be cool down by quenching system. Pretreated off-gas can be condensed or oxidize in catalytic incinerator. Endpoint of this technology can vary according to contaminant type and aim of the pilot test. System can be inertize by nitrogen which is got from one of supply units (nitrogen generator).

To verify designed parameters two sets of functional and operating test have been carried out. As an input matrices sand, soil and clayey soil were used. In the first set the „cold tests“ were carried out and in the second step „hot tests“ for process verification were carried out. Next is the last - third step for final verification with contaminated matrices as slightly contaminated soil and then the pilot plant could be used for testing the contaminated rubble or the filter cake.

CONCLUSION

DEKONTA has several types of units which can be used for testing of thermal desorption process. Pilot plant was developed based on results obtain from research project focused on thermal desorption optimization. Laboratory and semi-pilot tests are very important as shown on examples. During laboratory trials materials which can be processed by pilot plant were chose and risky materials as oil sludge which evolve methane, hydrogen and which tends to sinter were excluded so there is no danger coming out of the improper use of thermal desorption pilot plant.

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THE CONTENT OF HEAVY METALS IN THE SOILS OF DUMPS IN THE PROCESS OF RE-CULTIVATION, EASTERN HERCEGOVINA

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Soilsof dumps in the process of re-cultivation, the total content of heavy metals

ABSTRACT

The combustion of coal in thermal power plants is one of the major sources of environmental pollution due to the huge amount of ash deposited on soil near power plants, thereby causing soil contamination. Re-cultivationof soil is bringing the soil to a satisfactory condition after finishing the exploitation of mineral resources on the part of the soil where exploitation has been carried out, especially in terms of soil quality, growing agricultural plants, wildlife, natural habitats, water, forests and beneficial use of soil. The subject of this research is the site of "Dražljevo" where the ashes have been deposited since the first day of the commissioning of the mine and thermal power plant Gacko, eastern Hercegovina. Re-cultivation of ash dump Dražljevo was carried out in the early nineties, and the thickness of the buried layer of "humus" was about 45 cm.

The investigated sites are not contaminated with high content of total Cd, Pb, Cu and Zn, and their values are below the MAC. They are contaminated with a high content of total Ni, they are above the MAC and above the corrected limit value. The values of Cd and Cu at sites 1, 2 and 4 are above the corrected limit value. Mineralogical composition of the limestone substrate can be a source of geochemical origin of Cd, Cu and Ni, while the ashes of thermal power plants can be the cause of anthropogenic origin. The origin of the high concentrations of Cd, Cu and Ni can be objectively explained only after determining of readily available content which requires further research.

INTRODUCTION

In the process of operation,thermal power plants generate an enormous amount of ash that is usually deposited in its vicinity. These dumps occupy considerable areas of soil, which excludes the soil from the primary production. The subject of this research is the site of "Dražljevo" where the ashes have been deposited since the first day of the commissioning of the mine and thermal power plant in Gacko, eastern Hercegovina. Re-cultivation of ash dump Dražljevo was carried out in the early nineties, and the thickness of the buried layer of "humus" was about 45 cm.

Re-cultivation ofsoil is bringing the soil to a satisfactory condition after finishing the exploitation of mineral resources on the part of the soil where exploitation has been carried out, especially in terms of soil quality, growing agricultural plants, wildlife, natural habitats, water, forests and beneficial use of soil (Law on Mining of the Republic of Srpska). The concession contract (Article 9 of the same Law) defines the re-cultivation of the areas of degraded soils by performing concession activity, as well as other issues related to the exploitation of mineral raw materials. Mining project (Article 30) develops and analyzes the re-cultivation of soiland other terms that affect the evaluation of the technical, technological and economic justification of exploitation and performing mining activities.

Measures for correction of agricultural soil by meliorations include, among other measures, the re-cultivation of damaged and destroyed soils (Law on Agricultural Soil of the Republic of Srpska, Article 39, 2006).

Until 2015,Agriculture Development Strategy of Republic of Srpska defined measures of protection, utilization and correction of agricultural land i.e.the implementation of measures of re-cultivation and remediation of damaged and contaminated soils while respecting the regulations of the Law on Agricultural Soil.

Re-cultivation on the territory of BiH started to be applied during the second half of the fifties. Organized work on scientific research of re-cultivation began in mid-sixties, and the first field trial of re-cultivation that was methodically correctlyset dates back from 1966/67. The largest volume of re-cultivation was achieved in BiH in minesof Tuzla region (Vončina and Džindić, 1986).

Some of the soils are directly exposed to the influence of technogenic waste materials, which are deposited in the environment in the course of industrial processes, and which have a detrimental effect on the soil. As an example, there are many dumps that are mainly located close to factories, farms, mines and other facilities. The method of disposal of waste materials, in so far practice, leads to significant changes in the overall ecosystem of endangered area (Nešić et al. 2012).

The combustion of coal in thermo power plants is one of the major sources of environmental pollution due to the huge amount of ash, which is deposited into large pools near power plants, thereby causing contamination of soil and groundwater (Mandal and Sengupta, 2006).

Soil can be observed as a huge convector in which, under the influence of various chemical and biological processes, thesubstances, which are brought in, transform into such forms, i.e. compounds that may have useful effects. In these reactions, the formation of harmful compounds is possible too, which, if not avoided, could lead to the opposite effect - soil damage (contamination, degradation). Considering that the thermal power plants produce large amounts of waste, i.e. ash, and that ash has good chemical properties (pH, significant carbonate content and medium content of phosphorus and high potassium content), the ash must be handled carefully because it may contain some harmful ingredients, too, such as boron, molybdenum, copper and similar. (Resulović, 2003).

The aim of this study is to determine, by pedological researches,the total content of heavy metals cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), nickel (Ni) of soils of dumps in the process of re-cultivation for the purposes of obtaining an objective insight into the type, degree and damage to the soil.

MATERIALS AND METHODS

The totalcontent of heavymetalscadmium(Cd), lead (Pb), copper(Cu), zinc (Zn) andnickel(Ni), is determined ontheaveragesoil samples. Samples were collectedatfour sites of the dump Dražljevoat a depth of0-10cm.

The extraction of traces oftotal contentof heavy metals(BAS ISO 11047:2000, AAnalyst800,PerkinElmer, 2006, software WinLab32, version6.4.Rev.6), was performedin the laboratoryof the FederalAgro-Mediterranean Institutein Mostar, Bosnia andHerzegovina.

Fig. 1. Geografical position Gacko sity and Gatačko polje, eastern Hercegovina

Fig. 2. Thermal power plant and mineGacko

Fig. 3. Former Dražljevo ashes dump- today

RESULTS AND DISCUSSION

Used FBiH legislation according to the Law on Agricultural Soil (Official Gazette of FBiH, no. 52/09) i.e. the Instructions on determining the allowable amount of harmfuland dangerous substances in soil and methods of their investigation (Official Gazette of FBiH no. 72/09) treats pollution i.e. soil contamination with heavy metals in terms of growing the crop plants, i.e. as agricultural soil, based on textural characteristics.

The concentration of heavy metals in the soil, if it is significantly higher than normal, indicates the contamination either from anthropogenic sources or their natural geochemical origin. The control of their levels in soils occurs through comparisons with a maximum allowable concentration (MAC) for unpolluted soil.

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 maximum allowable concentration (MAC) of heavy metals in soils represent a significant foothold in the assessment of soil contamination by these mainly toxic elements. The limit minimal values are those values wherefunctional properties of the soil are fully achieved, i.e. they indicate the level at which a sustainable soil quality is reached. Remediation values are those values which indicate that the basic functions of soil areendangered or seriously impaired and require remediation, rehabilitation and other measures.

Limit values, remediation values and values that can point to significant contamination for heavy metals and arsenic, with the exception of antimony, molybdenum, selenium, tellurium, thallium and silver, depend on the clay content and / or organic matter in the soil. Correcting formula is used for heavy metals, depending on the type of soil on the basis of which the conversion is done:

$$(SW, IW)_b = (SW, IW)_{sb} \cdot \frac{A + (B \cdot \%\ gline) + (C \cdot \%\ organske\ materije)}{A + (B \cdot 25) + (C \cdot 10)}$$

(SW, IW) b - corrected limit or remediation value for particular soil,
(SW, IW) sb - limit or remediation value from the Regulation,
% Clay - the percentage of clay measured in a particular soil (particle size <2 μm),
% Organic matter - Percentage of organic matter measured in particular soil,
A, B, C - are constants dependent on the kind of metal.

Determining limit values is significant and is very important for the protection of health of people, and, in general, in the protection of wildlife (Kastori et al., 2003).

Tab. 1. The total content of heavy metals (mg / kg) of soils of dumps in the process of re-cultivation

Heavy metals (mg/kg)	Sites				MAC(mg/kg) (Official Gazette of RS, No. 88/2010)
	1	2	3	4	
Cadmium (Cd)	0.96	1.48	0.38	1.72	3
Lead (Pb)	63.90	61.20	67.63	59.50	100
Copper (Cu)	44.20	58.60	26.92	58.56	100
Zinc (Zn)	98.00	133.50	35.01	135.12	300
Nickel (Ni)	142.40	184.70	128.08	182.20	50

Tab. 2. The corrected limit and remediation values of total heavy metal content (mg / kg) of soils of dumps in the process of re-cultivation

Heavy metals	Corrected limit value (mg/kg)	Remediation value (mg/kg)
Cadmium (Cd)	0.66	9.96
Lead (Pb)	80.75	503.50
Copper (Cu)	33.48	176.70
Zinc (Zn)	137.20	705.60
Nickel (Ni)	37.80	226.80

Calculated corrected limit values and the remediation values of soilsof dumps in the process of re-cultivation are given in Tab. 2.
The total content of cadmium (Cd) in the soils of dumps in the process of re-cultivation ranged from 0.38 mg / kg at the site 3 to 1.72 mg / kg at the site 4. The total lead content ranged from 59.50 mg / kg at the site 4 to 67.63 mg / kg at the site 3. The total copper content ranged from 26.92 mg / kg at the site 3 to 58.60 mg / kg at the site 2. The total zinc content ranged from 35. 01 mg / kg at the site 3 to 135.12 mg / kg. The total nickel content ranged from 128.08 mg / kg at the site 3 to 184.70 mg / kg at the site 2 (Tab. 1).
The maximum allowable amount of cadmium (Cd) in soil is 3 mg / kg (Official Gazette of RS, no. 88/2010). The average content of cadmium in soils of Central Serbia is 0.805 mg / kg (The Report on the status 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), high content may be the resultof anthropogenic pollution (applicable in the industry, can be found in increased concentrations along the roads, as well as on arable land, as a result of intensive agrotechnics (from phosphoric fertilizers and some fungicides) (Adriano, 2001; Alloway, 1995). The investigated soils are not contaminated with cadmium, its content is below the MAC. The content of total cadmium on sites 1, 2 and 4 is above the corrected limitvalue, and all sites are far below the remediation values.
Maximum allowable amount of lead (Pb) in soil is 100 mg / kg (Official Gazette of RS, no. 88/2010). The average lead content in the soils of Serbia is about 40 mg / kg. The concentration is mainly increased along busy roads but also on soils formed on magmatic rocks, rich in metals (Report on the status of the soils in theRepublic

of Serbia, 2009). The soil is contaminated by industrial plants and motor vehicles burning gasoline to which Pb is added as an additive (Bytyqi and Sherifi, 2010). Limit values for lead are 100 mg / kg of soil (Scheffer and Schachtschabel, 1998). The investigated soils are not contaminated with lead, its content is below the MAC. The content of total lead at all sites is below the correctedlimit value, and far below the remediation value.

The maximum allowable amount of copper (Cu) in soil is 100 mg / kg (Official Gazette of RS, no. 88/2010). The average copper content in soils of Serbia is 27 mg / kg. There is the highest contamination of soil with copper in the vicinity of the mine of Bor and at Majdanpek, although there areindividual samples with high concentrations at other sites, too, occurring in some samples of soil under vine as a result of the application of copper preparations to protect the vines, fruits and vegetables, (The report on the status of soils in the Republic of Serbia, 2009). The investigated soils are not contaminated with copper, its content is below the MAC. The content of total copper at sites 1, 2 and 4 is above the corrected limit value, and all sites are far below the remediation value.

The maximally allowable amount of zinc (Zn) in soil is 300 mg / kg (Official Gazette of RS, no. 88/2010). The average zinc content in the soils of Serbia is 48 mg / kg. Zinc rarely occurs as a pollutant. On sandy, calcareous and highly acid soils, there is frequently deficit in zinc for plant nutrition (The report on the status of soils in the Republic of Serbia, 2009). The investigated soils are not contaminated with zinc, its content is below the MAC. The total zinc content at all sites is below the corrected limit value, and far below the remediation value.

Maximum allowable amount of nickel (Ni) in the soil is 50 mg / kg (Official Gazette of RS, no. 88/2010). The research results show that the average content of nickel in the soils of central Serbia is 58 mg / kg. High concentrations of Ni are found mainly in soils formed on rocks with a high natural content of this element, which are concentrated in the central and western part of Serbia, in mountain soils formed on serpentines (mainly in the humus-siliceoussoils). Previous research has shown that the nickel in the valley of the river of west Morava is of geochemical origin and that it is little soluble. A weak acidic reaction of these soils and harder accessible forms in which Ni is found reduce the risk of environmental pollution by this metal (The report on the status of the soils in the Republic of Serbia, 2009). The investigated soils are contaminated with nickel, its content is above the MAC for all studied samples. The content of total nickel at all of the sites is above the corrected limit value, and below the remediation value.

Limit values for heavy metals that are givenfor the soils with a high content of metals from geochemical sources, on the basis of which the suitability for use in agricultural production would be evaluated, should be greater than the limit value for the soils which contain heavy metals from anthropogenic sources (Antić-Mladenović, 2004).

Cadmium shows higher concentrations in soils over calcareous substrates in karst areas. Nickel, shows also increased concentration in soils over calcareous rocks in the Croatian karst area, with higher values mostly related to the soils of pastures and grass areas. In the continental part of the Croatia, higher concentration of nickel in soils of pastures was registered in Banovina. Ultramafic rocks, that naturally have an increased concentration of that element, are direct substrate of this soil. Concentrations of cadmium, nickel and copper,that are higher than it is provided by law,are mostly containedinpasture soils and grass surfaces above the carbonate lithologic units (Husnjak et al., 2010).

CONCLUSION

Based on the investigation results, it can be concluded that the studied sites are not contaminated with high content of total Cd, Pb, Cu and Zn, their values are below the MAC. They are contaminated with a high content of total Ni, all four samples of nickel were above the MAC.

In all investigated samples of the content of total Pb and Zn is below the corrected limitvalue. The content of total Cd and Cu is above the corrected limit value in samples at sites 1, 2 and 4. In all investigated samples, the total Ni content is above the corrected limit value. The contents of all investigated elements in the soil dumps in the process of re-cultivation are under remediation values.

Mineralogical composition of the limestone substrate can be the source of the presence of Cd, Cu and Ni of geochemical origin, while the ashes of thermal power plants can be the cause of anthropogenic origin. Origin of high concentrations of Cd, Cu and Ni can be objectively explained only after determining readily available content which requires further research.

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CONTAMINATED SITES IN INDIA: CHALLENGES AND RECENT INITIATIVES FOR MSW DISPOSAL SITES

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KEYWORDS
Contaminated Sites, India, Remediation, MSW Sites, Landfills

ABSTRACT

The sites contaminated by disposal of municipal solid waste pose a number of hazards to their surrounding environment. But the status of these sites is still unknown in India in terms of scale of size for planning the remediation effectively. The study tries to give an idea of the size of these sites for the cities having population more than a million.

Subsequently study attempts to present the challenges associated in remediation of these sites such as financial constraints and lack of standards in guidelines for clean-up. Recently, a number of initiatives have been taken in India to manage the municipal waste safely and cleaning-up the contaminated sites in collaboration with international agencies such as The World Bank and European Union. Government of India has started a program CBIMP (Capacity Building for Industrial Pollution Management) focusing on contaminated sites management. The study presents the scale of the size of the waste disposal sites, challenges associated in management of these sites and a glimpse of the recent initiatives being undertaken in India for clean-up.

INTRODUCTION

India's rapid economic growth and industrialization has led to serious concerns about pollution and waste generation. Industries such as petrochemicals, pharmaceuticals, pesticides, paints, dyes, fertilizers and mining generate hazardous waste. These toxic compounds/elements can bio-accumulate in plants and animals, eventually making their way to humans through the food chain, and also migrate to rivers and surface water bodies, as well as contaminating groundwater. The sites contaminated by disposal of municipal solid waste form an important component of contaminated sites in any region.

In India, 90% of the MSW is disposed in Uncontrolled MSW sites or commonly known as Dump sites (Kumar et al., 2009;Sharholy et al., 2008). According to census 2011, the total number of Urban Agglomerations/ Towns in India, which constitutes the urban frame, is 6166 in the country (Ministry of Home Affairs (MHA), 2011). Assuming on average three urban areas are serviced by a MSW site, there would be thousands of sites in India polluting surrounding environment. These dump sites are continuously polluting the environment around them and subsequently pose hazards to the communities in their vicinity (Mor et al., 2006; Pujari and Deshpande, 2005; Narayana, 2009; Singh and Dey, 2014). Furthermore, only a miniscule fraction of the disposal sites in India have engineered measures in place to protect environment and human health which makes the situation more severe. Initially these dumps are not a problem for the local government as these are far away from the communities and do not pose significant danger to the general public. But with manifold increase in population, the communities have expanded in and around these dump sites. A number of cities (bigger and smaller as well) have faced the protests from the nearby residents (Rao, 2014; Diggikar, 2014). So now it is becoming much difficult for the local as well as state and central government to ignore the threats from these dump sites. Remediation of these sites is fraught with challenges in India due to a number of constraints. However, recently a number of initiatives have been taken to start tackling the problem.

OBJECTIVE AND SCOPE

The objective of the study is to describe the status of MSW sites in India, challenges in their management and then to reflect on the recent initiatives and associated outcomes. The scope of the study is limited to MSW sites in Indian cities having more than the population of one million.

METHODOLOGY OF THE STUDY

The foremost step was the review of the literature regarding the information for the dump sites in India, from which the knowledge gap was evident. Thereafter, the offices of the municipal corporations in all 53 million plus cities were contacted with questionnaire regarding the status of dump sites under their jurisdiction. The questionnaires included questions such as number of disposal sites in each city (active as well as abandoned), base area, waste height and waste quantity for each of the sites. Information was also obtained from published literature, existing city reports, websites of municipal corporations and newspapers.For challenges and initiatives regarding remediation of these sites, literature survey and informal interviews with municipal corporations officials and experts working in the areas provided the required information.

STATUS OF MSW SITES OR DUMP SITES IN INDIA

For determining sizes, the dump sites were classified according to city population: 5-million plus cities (cities having population more than 5 million), 2-5 million cities (cities having population between 2 and 5 million) and 1-2 million plus cities (cities having population between 1 and 2 million).

There are eight cities in India having population of more than 5-million. Some of these cities also have waste processing plants which do not either operate at optimum efficiency or have other operational related issues such as complaints from neighbours about excessive pollution(Kumar et al., 2009; Nandi, 2015). The median area under these dump sites in 5-million plus cities is about 23-ha with a waste height (median) of 24m. The interquartile ranges (IQRs) for the base area and waste height are 15-65ha and 9-38m.

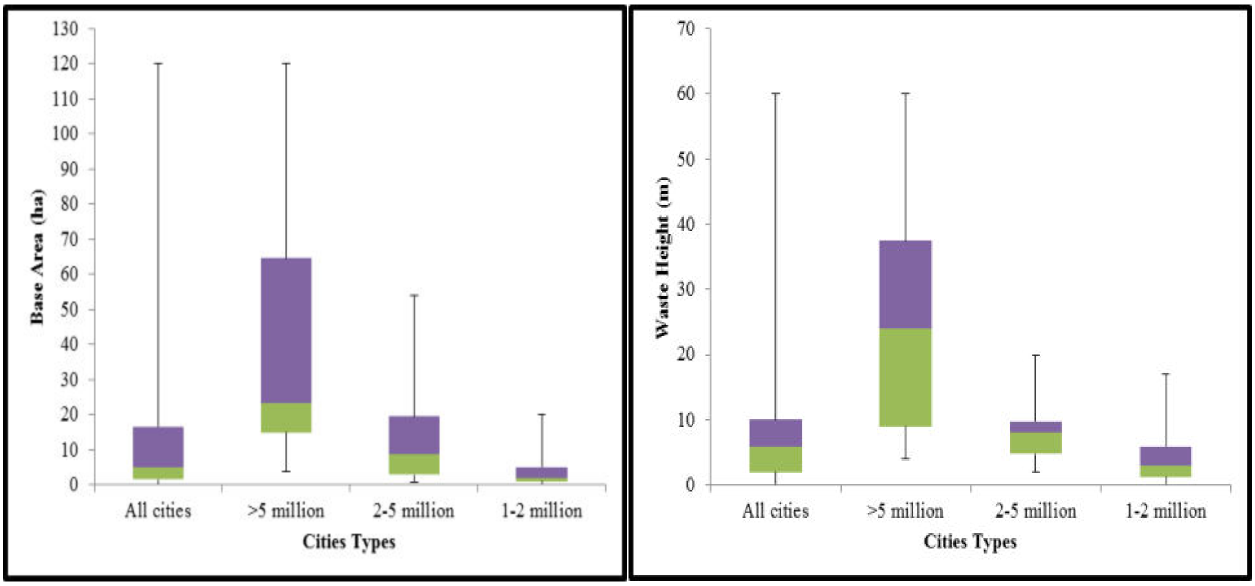

Fig. 1. Box and whisker plot for(a) base area and (b) waste height in dump sites in various categories of cities

There are eleven cities in India having population of between 2 and 5-million. Waste processing plants exist in a number of cities for Composting (e.g. Surat) and Refuse-derived-fuel (e.g. Jaipur). However, these plants run at very low efficiencies (Olivier, 2011; Singh, 2011; Chakraborty, 2014). Thus, most of the collected MSW from these cities is being disposed in uncontrolled landfills. Median area under these dump sites is about 9-ha (IQR 3 – 20 ha) and median height of waste is 8m in these dump sites (IQR 5-10m).

There are thirty-four cities in India having population between 1 and 2-million. Similar to bigger cities, on account of waste processing plants in defunct stage or running at very low efficiency, most of the collected MSW from these cities end up in uncontrolled landfills as (Sarkar, 2014; Nashik Municipal Corporation, 2011; Kumar, 2014). Median area under these dump sites is about 2ha (IQR 1-5ha) and median height of waste is 3m in these dump sites (IQR 1-6m).

CHALLENGES IN REMEDIATION

A number of challenges hamper the process of remediation in developing countries like India. Absence of planning tools such as ranking systems tailor-made for Indian conditions, lacuna in policy framework, and paucity of funds are some of the prominent issues.

Remediation of contaminated sites needs planning. The planning includes prioritization of the sites in terms of the hazard posed or cost/benefit analysis. A number of tools exist in other countries for prioritization of contaminated sites such as HRS-1990 (USEPA, 1990), RSS (Ministry for the Environment, 2004), RASCL (Golder Associates (NZ) Ltd, 2002) and JENV (Joseph et al., 2005). These tools rate the hazard posed by contaminated sites on a relative basis and the site with the highest hazard rating can be given the highest priority for closure/ remediation. India does not have such a ranking system to prepare a national priority list of contaminated list.

Furthermore, there may be a number of options available to control/remediate a site. The choice of a remedial action on a contaminated site depends on many factors e.g. site characteristics, contaminant characteristics, technical feasibility, environmental and user benefits and end use of the site (Promentilla et al., 2006). The appropriate technology will help reduce the residual risk, impact on workers and residents during and after implementation and the cost of cleanup. It will also maximize the environmental and other benefits. A number of Decisions Support Systems (DSS) exist in literature for selection of appropriate remediation technique. Decision support tools (DST) integrate data and report results in terms of simplified but representative decision information. A number of such DSS have been developed in developed countries e.g. DESYRE (Carlon et al., 2007); REC (Beinat et al., 1997). Some of these systems assist in cost estimation for remediation projects e.g. CARO and ROCO (Onwubuya et al., 2009). However, such systems have not been developed in India taking into consideration local conditions.

Having the baseline condition of dump sites is imminent for planning of remediation. This information is maintained in a number of developed countries. In USA, Environmental Protection Agency (USEPA) maintains a register of the landfills (remediated and prioritized for remediation) sites on its website (http://www.epa.gov); (USEPA, 1996). In France, a database of polluted sites and soils is maintained through BASOL database (EUGRIS, 2005). In Asia, Malaysia maintains an inventory of landfill sites in the country (Ministry of Housing and Local Government Malaysia (MHLG), 2005). In India, Central Pollution Control Board (CPCB) maintains the annual reports on MSW management as filed by various State Pollution Control Boards. But the information given in these reports is very brief and focuses on waste generation, collection and overview of treatment and disposal practices rather than the condition of dump sites. The absence of the basic information about the landfills in India further mars the planning process for remediation. This study tried to cover this gap in knowledge by elaborating on the sizes of dump sites in Indian cities.

The policy framework for management of contaminated sites in India is mainly limited to Environmental Protection Act, 1986 (MoEF, 1986) and Hazardous waste (Management, Handling and Transboundary Movement) Rules, 2008 (MoEF, 2008). The main responsibility for the formulation of environmental policy and regulations, and management of contaminated sites in India lies with the Ministry of Environment and Forests (MoEF), New Delhi. The Central Pollution Control Board (CPCB) is the authority mandated to implement environmental laws and guidelines at the national level. At the state level, the State Pollution Control Boards (SPCBs) implement the legislation by assessing pollution due to industrial or other anthropogenic sources. Other stakeholders in the management of contaminated land are the landowners, knowledge and research institutes (IITs, Research Labs), local government like municipalities, NGOs, Residents, Private Consultants, Contractors and technology vendors. The responsibilities of the stakeholders are not well-defined and does not help the situation. Moreover, there are no guidelines for the permissible limits of contaminants and, therefore, there is no sound, scientific basis for identifying a site as contaminated (GovilandDottridge, 2011). Also there are no guidelines regarding site assessment, selection of remediation technologies and design for implementation.

Funds and resources are a major hindrance in implementing the remediation of contaminated sites. Local governments do not have enough funds to carry out even the basic services like collection and safe disposal (Sharholy et al., 2008). The funds available are also not used in a planned manner leading to misuse and wastage of the resources. The MoEF formulated the latest environmental policy in 2006, where the Polluter Pays principle is mentioned for funding remediation of contaminated sites (MoEF, 2006). However, the liability is not well-defined. Furthermore, mechanisms for Cost recovery and securitization of assets from liable parties are not clearly mandated in Indian laws.

The lack of expertise is another major hindrance in the management of contaminated sites. In local governments, responsibility of solid waste management is generally assigned to a person of low competence (Guerrero et al., 2013) and even the personals are not specifically trained for such kinds of assignments. Other stakeholders such as CPCB and MOEF also have the shortage of experienced professionals for such kind of projects. The problem is even more severe in SPCBs. As of today, there are only two closure projects for MSW sites in India i.e. in cities of Delhi and Mumbai in India which have waste dump closed in a scientific manner with a gas collection system (UNFCCC, 2009; Datta, 2014). Thus professionals employed in these agencies also do not get the wide experience in such projects and are hesitant to take upon such projects. Furthermore, these projects have been recently completed and are still in trial phase. Thus there is also unwillingness to invest large sums of money and resources unless favorable results from these projects are available.

RECENT INITIATIVES

A number of initiatives have been taken up by the Indian government to start tackling the problem of contaminated sites. The most important initiative is with the help of World Bank in terms of monetary support. Some of the other recent collaborations and actions regarding management of contaminated sites have also been discussed in this section.

In year 2005, EU-India Action Plan Support Facility Programme (APSF) was launched (Mani and Bentinck, 2010). The project was funded by the European Union. The project implementation period was from December 2007 until June 2011. One of the thrust areas for the project was management of contaminated sites in India. The objectives of the project included enhancing the regulatory function and technical and institutional capacity of the Indian administration. The Project activities were confined to develop the policy dialogue between India and the European Union (EU) using advisory services, workshops, seminars and training. However, the program helped starting the dialogue and developing an overview of the status of contaminated sites in India. Also discussed were the requirements of funds, policy framework and capacity building for management of contaminated sites.

The World Bank also initiated a project involving Contaminated Sites known as “India - Capacity Building for Industrial Pollution Management”. The project includes technical assistance and investments to support two key areas: (i) Strengthening environment institutions through “learning by doing” and (ii) Investments in integrated pollution management (World Bank, 2006). Strengthening of environment institutions is being accomplished by technical assistance for the planning, monitoring and enforcement capacity of SPCBs and the other local Environment Departments in selected states. Specifically, technical assistance will be provided for developing a National Plan for Rehabilitation of Polluted Sites. Under the area of investments in integrated pollution management, investments are included to support for remediation of hazardous waste sites, promote voluntary compliance incentives and self-regulatory measures to improve performance and competitiveness of selected industrial clusters and support up-gradation of common environmental infrastructure. Investments supporting municipal solid waste management specifically includes remediation of dump sites; cleaning up and rehabilitation of land; improved land reuse and innovative institutional and financing models for integrated solid waste management. Under these projects opportunities to access Carbon Finance are also being explored where feasible.

Under the world bank project, three consortiums are working together to achieve various objectives: (i) Inventorization of contaminated sites in India (ii) Analysis of Remediation Technologies suitable in Indian context and for various types of contaminants (iii) Policy framework for management of contaminated sites. This is a very ambitious project and anticipates to vigorously start the process of contaminated sites’ management in India. However, according to the latest project update from world bank, the project activities continue to progress very slowly and are behind original schedule by more than two years. Considering the delays in bid processes and starting of remediation activities, the activities of the project are unlikely to be completed within the current project closing date (World Bank, 2015).

Recently Government of India has launched “SWACHH BHARAT ABHIYAAN” which emphasizes on the cleanliness in general. The mission seeks to achieve the goal of Clean India in next five years (Government of India, 2014). Although the mission is for the general cleanliness in one’s neighborhood, its effect may percolate into the contaminated sites management sector also.

Some initiatives have also been taken by a number of corporate houses e.g. the present study is part of a project sponsored by HUDCO, a semi-government entity engaged in urban rejuvenation in India. The project titled as “Development of a Contaminated Site Classification and Remediation System” focuses on MSW sites in India. The project aims to develop a system for ranking of MSW sites (Kumar et al., 2015).

CONCLUSIONS

The following conclusions may be drawn from the study:

- The dump sites of 5-million plus cities are much bigger in area and waste height than those in less populated cities.

  - The waste sites in 5-million plus cities are 23 ha in base area and 24m in waste height (median values). The interquartile ranges (IQRs) for the base area and waste height are 15-65ha and 9-38m.
  - Median base area for dump sites in 2-5 million cities is 9 ha (IQR 3-20ha). The median waste height is 8m (IQR 5-10m).
  - The waste sites in 1-2 million cities are on median 2 ha in area (IQR 1-5ha) and about 3m in height (IQR 1-6m).
- A number of challenges such as absence of planning tools such as ranking systems tailor-made for Indian conditions, lacuna in policy framework, paucity of funds, and lack of expertise and experience with remediation technologies, hamper the process of remediation of contaminated sites in India.
- A number of initiatives have been taken up with the help of international agencies e.g. The World Bank, EU. These issues have opened up the issue and made a breakthrough in the process of contaminated sites' management. However, implementation on ground still remains a challenge.

ACKNOWLEDGEMENT

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POSTER SECTION

INTERNATIONAL CONFERENCE CONTAMINATED SITES BRATISLAVA 2015

27 –29 MAY, 2015

27 –29 MAY, 2015		
Nr.	**Presenter/ Name Surname**	**Poster Title**
1	**JAN BARTOŇ**	SOIL AND WATER SAMPLING AND ANALYSIS PROGRAM IN KOSOVO
2	**MARINO A.**	ESTIMATING CLEAN-UP COSTS ACCORDING TO SITE-SPECIFIC CONDITIONS AND TECHNOLOGIES TO BE APPLIED
3	**ELENA BRADIAKOVÁ**	EDUCATION AND PUBLIC AWARENESS AS A SUPPORT IN CONTAMINATED SITES REMEDIATION IN SLOVAKIA
4	**KATARÍNA DERCOVÁ**	BIOSTIMULATION AND BIOAUGMENTATION OF PCBs
5	**HANA DUDÁŠOVÁ**	ELIMINATION AND TOXIC EFFECTS OF POLYCHLORINATED BIPHENYLS IN REAL CONTAMINATED SEDIMENT
6	**ZUZANA ĎURIANČÍKOVÁ**	INTEGRATION OF THE PUBLIC INTO THE CONTAMINATED SITES REMEDIATION
7	**JURAJ GAVORA**	MANAGEMENT OF SITES CONTAINING POPs MIXTUREs OR PESTICIDES IN THE SLOVAK REPUBLIC
8	**MICHAL JANKULÁR**	PRELIMINARY EVALUATION OF GROUND WATER QUALITY IN THE SURROUNDING OF LEACH RESIDUE PILE NEAR SEREĎ CITY (SLOVAKIA)
9	**DALIBOR JOVANOVIC**	APPLICATION OF HYPOCHLORITE SOLUTIONS IN REMEDIATION OF SURFACES CONTAMINATED BY BLISTER CHEMICAL AGENTS
10	**RENÁTA FĽAKOVÁ**	THE WATER QUALITY OF GRAVEL PITS AND THE DANUBE RIVER IN THE URBANIZED AREA OF BRATISLAVA (SLOVAKIA)
11	**RADOVAN KARKALIĆ**	DECONTAMINATION OF HIGHLY TOXIC CHEMICALS THICKENED FORMULATIONS AT DIFFERENT SURFACES
12	**JAKUB KOSTECKI**	THE POSSIBILITY OF THE HYBRID POPLAR USE IN THE SOIL PHYTOREMEDIATION PROCESS

27 –29 MAY, 2015		
Nr.	**Presenter/ Name Surname**	**Poster Title**
13	**PETR LACINA**	PRACTICAL APPLICATIONS OF FERRATES (Fe^{VI} AND Fe^{V}) IN COMBINATION WITH HYDROGEN PEROXIDE FOR FAST AND EFFECTIVE REMEDIATION OF CONTAMINATED GROUNDWATER
14	**KATARÍNA LÁSZLOVÁ**	THE COMPARISON OF BIOLOGICAL DEGRADATION OF POLYCHLORINATED BIPHENYLS AND PHYSICO-CHEMICAL METHODS OF THEIR ELIMINATION
15	**LUCIA LACHKÁ**	ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS CONTAMINATION IN URBAN TOPSOILS OF BRATISLAVA
16	**ANDREJ MACHLICA**	CHZJD LANDFILL IN VRAKUNA – THE SLEEPING LOAD OF BRATISLAVA
17	**SIMONA ŠKULTÉTYOVÁ**	IMPACT OF CALCIUM AND MAGNESIUM ON HEALTH STATUS (SLOVAK REPUBLIC)
18	**PAVEL ŠPAČEK**	TWO PROGRESSIVE PROCEDURES FOR CONTAMINANT REMOVING FROM THE SUBSURFACE AND A NON-INVASIVE METHOD OF CONSTRUCTION SUBSURFACE CLEANING
19	**IRINA PERELOMOVA**	TOXIC EFFECTS OF TRACE ELEMENTS ON MALE REPRODUCTIVE HEALTH
20	**PAVOL MIDULA**	HEAVY METAL CONTAMINATION IN WATER AT LIBIOLA ABANDONED COPPER MINE
21	**KATARÍNA PALUCHOVÁ, JAROMÍR HELMA**	ESTABLISH THE GEO-DATABASE ON ECOLOGICAL HEALTH OF THE MILITARY SITES
22	**THOMAS HAUERBERG LARSEN**	THERMAL EXPERIENCES IN DENMARK
23	**MARIJANA MARKOVIĆ**	UTILIZATION OF AOPS FOR DEGRADATION OF EMERGING CONTAMINANTS AND REACTIVE DYES
24	**CLAUDIA NECULAU**	THE UCB SITE IS POLLUTED IN ACID TAR
25	**PETER MEDVED**	NO NET LAND TAKE BY 2050 – REALITY OR SCIENCE FICTION FOR MUNICIPALITIES

SOIL AND WATER SAMPLING AND ANALYSIS PROGRAM IN KOSOVO

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KEYWORDS
Contamination, Investigation, Groundwater, Thermo Power Plant, Kosovo

ABSTRACT

The main objectives of the investigation were to identify contaminated sites caused by Termo Power Plants and their Ash Dumps which is located near the city of Oblic/Obiliq some 10 km to 20 km from Prishtina, the capitol of the Republic of Kosovo.

The assignment includes the following major tasks: Sampling and analysis of ground water, surface water, waste water, river sediments and soil, drilling/construction of groundwater monitoring wells and reporting, preparation and related services (e.g. flow rates measuring).

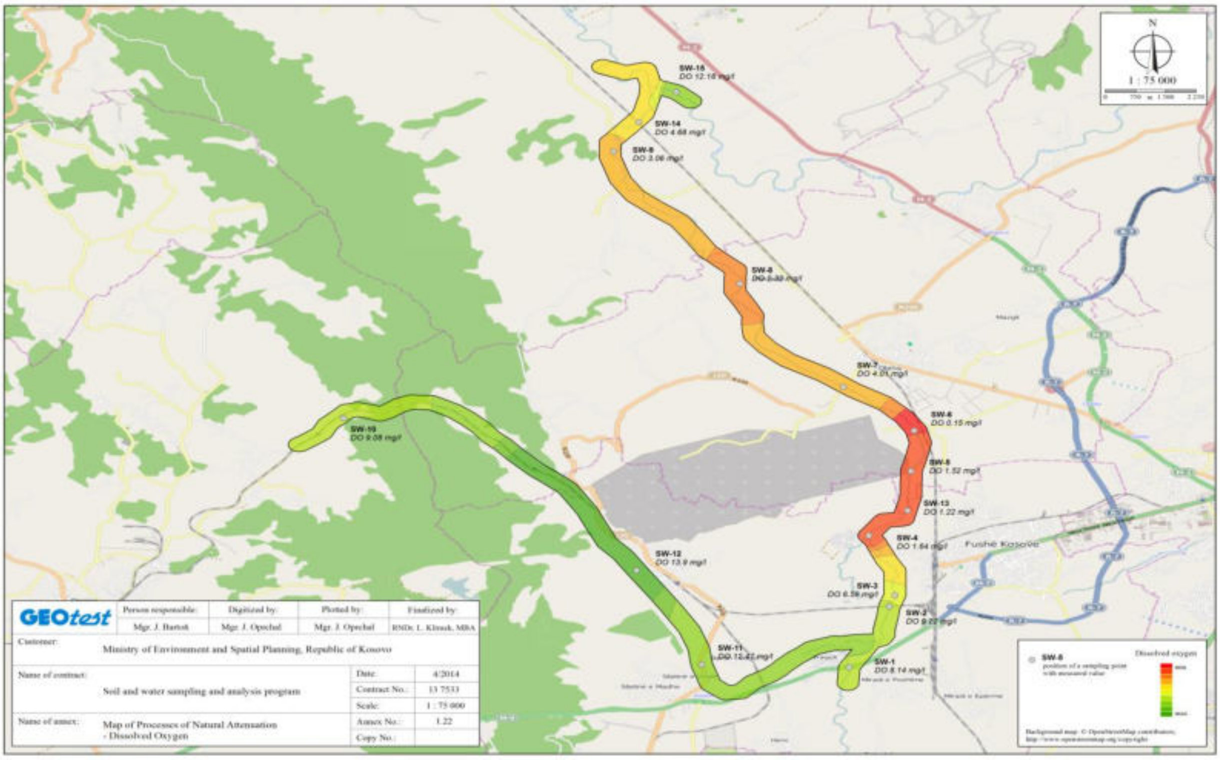

Fig. 1. Map of Dissolved Oxygen in the river Sitnica and tributaries

GEOtest, a.s. was commissioned by the Ministry of the Environment and Spatial Planning of the Republic of Kosovo to perform Soil and Water Sampling and Analysis Program in Kosovo.

The area selected for lignite based power generation and lignite extraction is located near the city of Oblic/Obiliq some 10 km to 20 km from Prishtina, the capitol of the Republic of Kosovo.

The assignment includes the following major tasks: Sampling and analysis of ground water, surface water, waste water, river sediments and soil, drilling/construction of groundwater monitoring wells and reporting, preparation and related services (e.g. flow rates measuring).

The results were compared with the limits applicable in the EU and, based on this, sites were identified, in which excessive contamination was detected.

Within the survey, sources of contamination were identified – these are Thermo Power Plants (TPP A, TPP B) and their Ash Dumps, Waste Dump and Mining Area, but also significant local sources of contamination – these are particularly Romani settlements and plants (operating facilities) in villages and towns, which are located in them (car washes, a fire station, small workshops, car repair shops), non-functional waste management (wastes are gathered chiefly around water streams by bridges and directly in rivers and creeks – waste water) and the lack of WWTPs (sewer lines are also terminated in water streams).

Based on the results of laboratory analyses and the overall view of the site concerned, it is possible to recommend the following steps for sustainable and environmentally sound operation of thermal power plants:

- To equip the existing thermal power plants with more advanced technologies, i.e. to renovate TPP A and TPP B ; or to replace the plant(s) with a new plant all in compliance with latest EU standards.
- To improve waste management in the whole area.
- To commence construction of treatment plants of waste industrial and household water.
- To install a network of monitoring boreholes and to carry out their regular monitoring.
- To check landfills for possible leakage.
- To control the correct technology of mining and waste water handling.
- Based on the monitoring actions realize detailed additional survey of hot-spots.
- Based on the additional hot-spots survey plan realize remediation actions where needed.

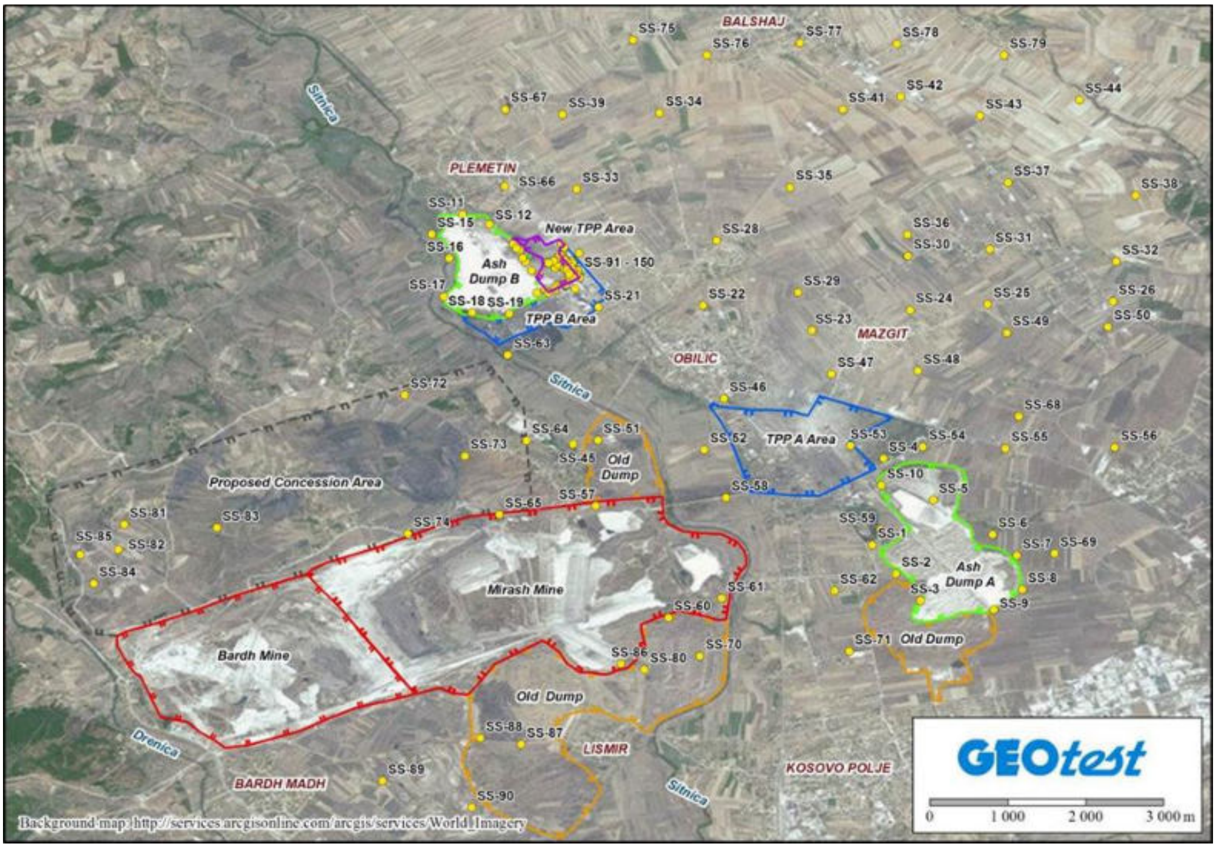

Fig. 2. Map of Soil Samples

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ESTIMATING CLEAN-UP COSTS ACCORDING TO SITE-SPECIFIC CONDITIONS AND TECHNOLOGIES TO BE APPLIED

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KEYWORDS
Remediation, contaminated sites, groundwater, risk assessment, cleanup cost

ABSTRACT

This article reports about steps needed in order to develop cost estimates during feasibility studies, including aspects connected to the alternative remediation techniques, which should be applied while respecting safety criteria provided for workers (including remediation operators) and residents.

When site-specific information is available about a site to be cleaned up, costs can be estimated by using a site-specific approach, which generally provides more reliable estimates in comparison with other kinds of approaches. In spite of it, it requires at the same time the highest level of information about polluted sites. Where enough site-specific information about a polluted site is available (especially about contamination nature and extent), the latter can be directly used in order to build a sound cost estimate.

The uncertainty of site-specific cost estimates is up to the level of project definition, including nature and extent of contamination, migration ways and targets, as well as feasibility of remediation technologies. Anyway, some uncertainty must be considered, even when site-specific information is available, because nobody is able to predict definitely every technical, legal, administrative situation which can occur during a remediation process.

ARTICLE

According to the level of investigation and remediation which is carried out at contaminated sites and according to the available information about them, cost estimations can be developed by using detailed (site-specific) or parametric approaches, based on measures or on literature. Detailed approaches generally provide more reliable and defendable cost estimations, more probably approaching the real clean-up cost; in spite of it, they require the highest level of information about the sites to be cleaned up.

Of course, even cost estimates deriving from detailed approaches are characterized by some uncertainty, up to the level of projects definition. Cost estimations concerning sites where a remediation system is already existing are in fact less uncertain than cost estimations concerning sites where remediation has only been suggested or where several options are still on evaluation (i.e., during feasibility studies).

As soon as enough site-specific information has been known, it is possible to start developing a detailed (bottom-up) approach in order to estimate costs which are connected to a clean-up intervention.

Regardless of the approach which the estimator can choose (either detailed or parametric), the necessary steps to be followed during feasibility studies, in order to develop every good cost estimate related to a clean-up alternative, should be the following ones:

1. Description of the remedial system to be applied
2. Identification of cost element structure, distinguishing between capital, annual and periodic costs
3. Addition of contingency
4. Estimate of other costs (for services, for controls from Institutions…)
5. Passage from present value analysis to sensitive analysis
6. Review

The first step is strictly connected to the remedial alternative to be applied, thus it is important at this stage to describe at a general way the interested remedial alternatives and to focus attention on aspects related to them, such as nature and extent of contamination to be treated as well as costs related to the technique, year after year.

About the remedial alternatives which could be taken into account, during the last years at INAIL/DIT we carried out some studies about techniques which are generally applied to clean up contaminated sites (concerning both groundwater and soils).

The second step of a good cost estimate is then identification of the cost element structure associated to the considered alternative. Such a kind of structure should consist in separated sub-structures including capital, annual and periodic costs, each one including cost elements concerning construction activities, maintenance, monitoring, other services and institutional controls.

An important factor which should be always considered in carrying out a cost estimate is surely contingency, in order to cover unknown and unforeseen circumstances which cannot be evaluated at the time of the estimate itself. Taking into account of contingencies should be the third step of cost estimate processes. Contingency can be related to scope or to bid. Scope contingency covers unknown costs due to changes in scope, which might occur during design; for this reason, scope contingency decreases while project is going on. Bid contingency covers unknown costs associated with constructing or implementing a given project scope.

The successive step should be including costs for professional and for technical services (project management, remedial design, construction management and technical support) as well as costs related to institutional controls ended to reduce or minimize exposure to site contamination or hazards by limiting or restricting site access: i.e., institutional control plans, restrictive covenants, property easements, zoning, deed notices, advisories, groundwater use restrictions, and site information database.

Institutional controls are project-specific costs and they can be also an important component of a remedial alternative. This is why they should be generally separated from other costs in estimate process, better if they are considered on a sub-element basis. Institutional controls may need to be updated or maintained, either annually or periodically.

A present value analysis, successive step of cost estimate, can allow to compare different remedial alternatives according to the present value of capital, annual and periodic costs. Further step is sensitivity analysis, such a type of uncertainty analysis which is going to measure the project impact whenchanging one or more input values. While developing a remedial alternative costestimate, sensitivity analysis should be taken into account for those factors having a relatively high degree of uncertainty and that, with only a small change in their value, could significantly affect the overall cost of the considered alternative.

As it has been more times underlined, cost estimates are always characterized by some uncertainty, and a sensitive analysis performed at the end of an estimating process in order to focus attention on more factors giving more uncertainty and that, with only a small change in their value, could significantly affect the overall cost of the project. By the way, even contingency is one of the most recommended common methods for factoring uncertainty into a cost estimate.

Factors to be considered in cost sensitivity analyses for remedial alternatives include: volumes of contaminated material and their degree of contamination; possibility that a clean-up system could be unsuccessful and, as a consequence of it, some extra costs could be necessary in order to replace the failed system or some of its parts; time required for the remedial action (the longer is the duration of treatments, the higher is the importance of such a factor); discount rate, in order to investigate uncertainty concerning future economic conditions. The importance of sensitivity analysis is due to the possibility to identify, because of it, the critical factors of a remediation design.

The last step in the cost estimate process for a remedial alternative is its revision. It is generally carried out with the help of some opportune checklists.

CONCLUSION

Estimators who must develop cost estimates during the early stages of clean-up processes can take into account of limited information. Such an information must be enough to support for their decisions.

Of course, in order to develop some more complete and accurate clean-up cost estimates by following the steps described as in this paper, it could be more preferable to base own cost estimate upon site-specific approaches, instead of using parametric approaches, in order to decrease uncertainty related to the estimate itself.

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Investment into Your Future!
Education and public awareness as a support
in contaminated sites remediation in SR
The project is co-financed by the European Union Cohesion Fund
within the Operational Programme Environment

EDUCATION AND PUBLIC AWARENESS AS A SUPPORT IN CONTAMINATED SITES REMEDIATION IN SLOVAKIA

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KEYWORDS
contaminated sites, project, awareness, education, publications

SLOVAK ENVIRONMENT AGENCY PROJECTS RELATED TO CONTAMINATED SITES

The project entitled ‘Education and public awareness as a support in contaminated sites remediation in Slovakia’ (the Awareness Project) is the latest in a series of Slovak Environment Agency (SEA) projects that address contaminated sites (CS). The Awareness Project follows from the last three projects in the series:

1. the pilot project, a geological task entitled The Systematic Identification of Contaminated Sites in the Slovak Republic (2006–2008)
2. Regional Studies of the Environmental Impacts of Contaminated sites in Selected Regions(2008–2010)
3. The Upgrade of the Information System of Contaminated sites (2009–2014)

Project Awareness’s chief activities have been focused on educating and raising the awareness of state and public administration and integrating the Information System of Contaminated sites (ISCS) with other related registers, primarily those of the Ministry of Environment of the Slovak Republic (MESR). The groundwork for the ISCS was laid as part of the pilot project from 2006 to 2008.

ACTIVITIES AND TARGET GROUPS OF THE AWARENESS PROJECT

The Awareness Project’s primary activity is to inform the public about and promote the issue of contaminated sites, including its remediation. The target groups of the project’s educational and promotional activities are chiefly the staff of public and state administration, owners of contaminated sites, experts on contaminated sites from practice and scientific research institutions, qualified professionals in the field of CS and professionals in environmental education. Educational and promotional events focused on contaminated sites are held throughout all eight of Slovakia’s regions: the Bratislava, Trnava, Trenčín, Nitra, Banská Bystrica, Košice and Prešov regions.

IMPLEMENTED ACTIVITIES

The activities of the Awareness Project are generally defined as informing the public about and promoting the issue of contaminated sites. The project is currently being implemented in part by certain activities within the State Programme for the Remediation of Contaminated Sites for 2010–2015, particularly as part of Objective 1: Improving the management of contaminated sites by encouraging recognition of the problem and legitimising contaminated sites policy through educational/awareness-raising measures. As part of Project Awareness, the following activities have been implemented to date through a package of conference and professional seminars focused on CS:

1. Seminar for owners of contaminated sites
Venue: Hotel Dixon, Banská Bystrica
Date: 27 February 2013
Number of participants:77

2. International conference: Contaminated Sites Bratislava 2013

INTERNATIONAL CONFERENCE
CONTAMINATED SITES
BRATISLAVA 29–31 MAY 2013

Fig. 1. The participants of the ICCS Bartislava 2013 – Common Forum members – outside the Presidential Palace in Bratislava.

Venue: Hotel Tatra, Bratislava
Date: 29–31 May 2013

Over its three days, the conference was attended by 261 participants from 27 countries, predominantly from Europe, but also from Asia and America. Presentations were divided into six topically moderated sections, with a total of 28 papers delivered over two days. Papers from other authors were presented via 24 posters. After the presentations were given, the afternoon of the third day was devoted to a tour of the Slovnaft, a. s. refinery in Bratislava-Vlčie Hrdlo.

The conference also included a separate two-day work meeting between representatives of member countries of the Common Forum on Contaminated Land in the European Union. The Common Forum Secretariat, headed by Ms Dominique Darmendrail, is based in Orléans, France (www.commonforum.eu).

Contaminated Sites Bratislava 2013 was also attended by a group of distinguished guests sponsored by the FAO Regional Office for Europe and Central Asia – REU, including countries of the former Soviet Union. This organisation has its headquarters in Budapest (http://www.fao.org/europe/reu-home/en/).

The papers of individual conference participants are available in print in the over 200-page conference proceedings. More information on Contaminated Sites Bratislava 2013, including the electronic version of the proceedings, photographs of the conference and most of the presentations, is available at http://contaminated-sites.sazp.sk/.

3. Seminar for professionals qualified in the field of contaminated sites

Venue: Hotel Barónka, Bratislava-Rača
Date: 25 June 2013
Number of participants: 90

4. ŠIŠKA: a trade show of environmental education programmes

Venue: Hotel Royal, Látky-Prašivá
Date: 17–19 October 2013
Number of participants:140

5. Seminar for owners of contaminated sites

Venue: Agroinštitút Nitra, š. p., Nitra
Date: 22 October 2013
Number of participants:70

6. International conference Contaminated sites Štrbské Pleso 2014

Venue: Hotel Sorea Trigan, Štrbské Pleso, Vysoké Tatry
Date: 23–25 April 2014
Number of registered participants: 100

The international Czech-Slovak conference **Contaminated sites** Štrbské Pleso 2014 was held from 23 to 25 April 2014 at the Sorea Trigan Hotel in Štrbské Pleso under the auspices of the Ministry of Environment of the Slovak Republic. Over its three days, the conference was attended by a total of 285 participants (87 + 100 + 98) from the Czech and Slovak republics.

7. Seminar for state administration staff on contaminated sites

Venue: Hotel Sorea Regia, Bratislava
Date: 13 May 2014
Number of participants: 99

Fig. 2. The participants of the seminar for state administration staff on contaminated sites in Bratislava, 13 May 2014.

8. Seminar for owners of contaminated sites

Venue: Hotel Sorea Trigan, Štrbské Pleso
Date: 30 September 2014
Number of participants: 72

9.**Presentation Day** on CS issue:

Venue: Hotel Lux, Banská Bystrica
Date: 17 March 2015
Number of participants:99

The project's package of publications focused on CS has to date included:

1. Pamphlets for professionals and the general public

The Awareness Project has included the publication of the informational pamphlets *Environmentálne záťaže na Slovensku – Základné informácie pre odbornú verejnosť* '[Environmental burdens (Contaminated sites) in Slovakia: Basic Information for Professionals] and *Environmentálne záťaže na Slovensku – Základné informácie pre laickú verejnosť* [Environmental burdens (Contaminated sites) in Slovakiain Slovakia – Basic Information for the General Public]. Both have the goal of providing basic information on the issue of contaminated sites in Slovakia, presenting the most important concepts, an overview of the pertinent legal norms, data on the ISCS, possible means of financing the handling of CS and other sources of information. The pamphlet for professionals has also been published in English under the title *Environmental Burdens in Slovakia – Basic information for professionals*.

2. Publications for the school programme Enviróza (Envirosis)

Fig. 3. The Envirosis logo.

For participants in the school game Envirosis, three publications are available in print and electronic form: The *Teacher's Handbook* is a companion to implementing the programme's basic phases; the *Worksheets for Primary and Secondary Schools* feature 50 activities for pupils and students, divided into five subject areas (Contaminated sites, Classes of Contaminated sites, Water, Soil and Bedrock, Human Health); the *Information pamphlet* provides basic information about the school game. The school programme Envirosis is accessible at http://www.enviroza.sk.

3. Conference proceedings

The published proceedings of both conferences are available electronically at http://contaminated-sites.sazp.sk/.

4. The publication *Management of Contaminated sites in Slovakia*

Published in Slovak and English, this 80-page publication imparts the latest information on handling contaminated sites in Slovakia, with an emphasis on current legislation, academic education and research, environmental education, the finalisation of the CS Information System and the implementation of projects within the Operational Programme 'Environment'.

5. A 120-page **environmental magazine** is being prepared for publication in April or May 2015, providing space primarily for wide information for general publicrelated to the management of CS in Slovakia including remediation projects implemented as part of the Operational Programme 'Environment'.

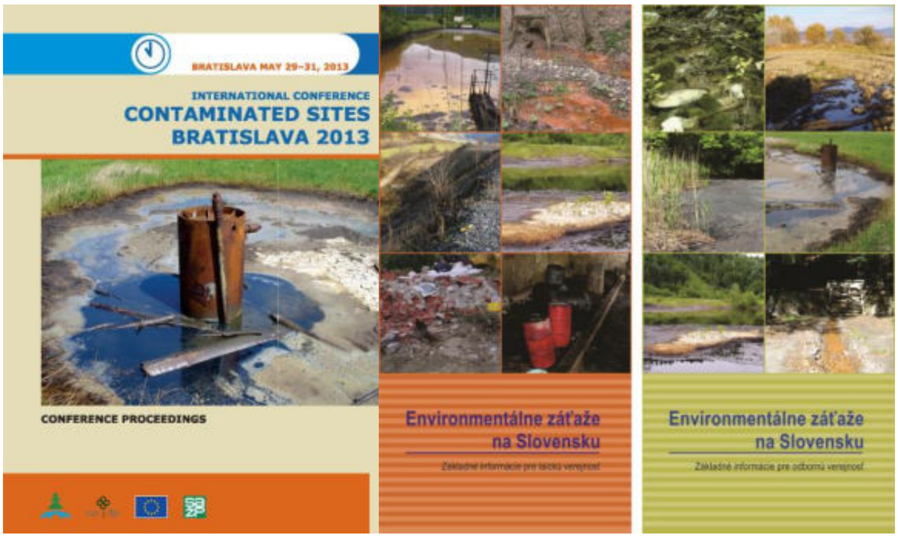

Fig. 4. The ICCS Bratislava 2013 conference proceedings and the pamphlets Environmental burdens in Slovakia.

School programmes make up a separate group:

1. A school programme (competition) focused on the mapping of selected contaminated sites entitled Envirosis uses an innovative outdoor game – based on the the rules of geocaching – to acquaint the young generation with the issue of contaminated sites. Specifically, it is focused on the mapping of selected contaminated sites – waste disposal sites, dunghills, fuell stations, industrial areas and mineral extraction (mining) areas – which contaminate the local environment. The programme is aimed towards pupils at the second level of primary school and in secondary school, as well as their teachers. The programme's first edition had its ceremonial opening at ŠIŠKA, a three-day trade show of environmental education programmes held 17–19 October 2013 at the Royal Hotel in Látky-Prašivá.

The three winning teams of the programme's first editions were awarded with field trips:

1. First place (Greenpeaces from Topoľčany): Komárno (the Old and New Fortress) and the Dropie Environmental Education Centre, 2 October 2014, 2. Second place (Snežienky [The Snowdrops] from Poprad): the mine in Novoveská Huta + the Levoča UNESCO World Heritage Site, 17 September 2014,

3. Third place (Krúžok Dobrovoľník Anjel [The Angel Volunteer Club] from Stará Ľubovňa + Tajkáči Poprad): the slag heap in Žiar nad Hronom + the mining trail in Špania Dolina, 22 September 2014

The first edition of Envirosis also included three accompanying competitions: the Sci-Fi competition for best science-fiction story, the Info competition for best informational video and the PhotoBurden competition for the best photograph.

The 2014/2015 edition of the outdoor game was launched with a modified methodology.

The school programme Envirosis is implemented under the auspices of the Ministry of Environment of the Slovak Republic. Envirosis's mascot is Ecoterium, a cute and helpful little monster created by Mgr. Ladislav Vojtuš, PhD. More information on the game is available at www.enviroza.sk.

2. EnviroQuestions 2013/2014: a mail-in environmental knowledge challenge

Announced in February 2014, EnviroQuestions (EnvirOtázniky) 2013/2014 was the 9th edition of the environmental knowledge challenge for pupils at the second level of primary school. With contaminated sites as its central theme, the challenge consisted of 10 questions from each of the following topics: 1. Contaminated sites, 2. The Envirosis school programme, 3. Types of contaminated sites, 4. Soil and Bedrock, 5. Water and 6. Human health. The deadline for entries was 30 April 2014. More information on the challenge's 9th edition is available at www.envirotazniky.sk.

The production of a short film and video spots

Work is currently being done on the production of a 30-minute film entitled *Contaminated sites in Slovakia*, devoted to the current state of efforts to address CS in Slovakia. Six video spots warn viewers of the health and environmental risks of CS, each focusing on one of the most common environmental pollutants related to CS: 1: arsenic, 2: mercury, 3: benzene, toluene, ethylbenzene and xylenes, 4: polychlorinated biphenyls, 5: chlorinated aliphatic hydrocarbons – dichloroethene, trichloroethene, tetrachloroethene and vinyl chloride, 6: pesticides.

Fig. 5. Envirosis's mascot Ecoterium, a cute and helpful little monster, has been cleaning and tidying contaminated sites tirelessly.

ACKNOWLEDGEMENT

This project is financially supported by the Cohesion Fund of the European Union within the Operational Programme 'Environment' (2007–2013).

BASIC INFORMATION ON THE PROJECT 'EDUCATION AND PUBLIC AWARENESS AS A SUPPORT IN CONTAMINATED SITES REMEDIATION IN SLOVAKIA'

Source of funding:the Cohesion Fund of the European Union within the Operational Programme 'Environment'(2007–2013)

Duration: June 2012 to May 2015
ITMS project code: 24140110232
Amount of the non-repayable grant: € 419,716.04
Main objective: Raising the general public's awareness concerning the issue of addressing contaminated sites, including its remediation
Specific objectives: Making the public more informed about contaminated sites
Project manager: Ing. arch. Elena Bradiaková
Address: Slovak Environment Agency
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Telephone: + 421 48 43 74 164
E-mail: elena.bradiakova@sazp.sk
Web: http://www.sazp.sk/public/index/go.php?id=2365

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OSVETA, PRÁCA S VEREJNOSŤOU AKO PODPORA PRI RIEŠENÍ ENVIRONMENTÁLNYCH ZÁŤAŽÍ V SR

PRIPRAVOVANÉ AKTIVITY V R. 2015

• PREZENTAČNÝ DEŇ

Miesto konania: Hotel Lux Banská Bystrica
Termín konania: 17. marec 2015
Plánovaný počet účastníkov: 100

V rámci prezentačného dňa predstavíme výsledky projektu Osveta, práca s verejnosťou ako podpora pri riešení environmentálnych záťaží v SR. Súčasťou prezentačného dňa bude výstava posterov informujúcich o jednotlivých projektoch SAŽP v oblasti EZ v rámci Operačného programu Životné prostredie, ktorých aktivity a finančné čerpanie je potrebné uzatvoriť do konca roka 2015. Prezentačný deň prinesie aktuálne informácie o novom Operačnom programe Kvalita životného prostredia (2014–2020) a príklady úspešných projektov podporených OPŽP (2007–2013).

- Prihláška/návratka na prezentačný deň
- Program
- Pozvánka

• Vydanie publikácie Riešenie enviromentálnych záťaží na Slovensku

Publikácia, ktorú pripravujeme v slovenskom a v anglickom jazyku, na 80 stranách prinesie aktuálne informácie v oblasti riešenia

Fig. 6. Print screen of the Awareness projects' website.

BIOSTIMULATION AND BIOAUGMENTATION OF PCBS

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KEYWORDS
Bioaugmentation, biostimulation, PCBs, surfactants

ABSTRACT

The study is focused on biodegradation of polychlorinated biphenyls (PCBs) in contaminated sediments using the perspective and prospective biostimulation and bioaugmentation approaches of bioremediation. Isolation and identification of well adapted PCB-degrading bacterial strains using 16SrRNA method from long-term PCB-contaminated sediments sampled from the surroundings of the former PCB factory represented an important part of the obtained results. Biodegradation of PCBs was performed with addition of the individual bacterial strains or artificially prepared consortia in the sterile or non-sterile sediment to study synergistic or competitive effects of inoculated and the indigenous microorganisms. The results obtained indicated beneficial effect of both biostimulation (addition of nutrients or surfactants) and bioaugmentation (addition of bacteria) approaches on the biodegradation of PCBs. Both approaches depended on the presence or inoculated bacteria, their amount, viability, and degradation ability. Under the applied conditions, the highest degradation was observed using bioaugmentation approach in the presence of a single strain *Rhodococcus* sp. or a bacterial consortium containing *Rhodococcus* sp., *Starkeya novella*,and *Achromobacter xylosoxidans* and with the biostimulation approach using the increased amount of nutrients (nitrogen and phosphorus) and oxygen. Bioaugmentation with *Stenotrophomonas maltophilia* in combination with biostimulation using addition of the synthetic surfactants Tween 80/Triton X led to an increased elimination of all evaluated PCB congeners. The ecotoxicity of biotreated sediments was substantially lower than that of the untreated. Data obtained using real PCB-contaminated sediment might be useful in the preliminary design of a site-specific bioremediation strategy.

I. INTRODUCTION

Degradation of PCBs is the major environmental concern regarding the contamination of soil and groundwater, as well as potential hazardous effects on human health. Since PCBs are hydrophobic, they partition preferentially to organic particles in the environment that serve both as long-term reservoirs and as carriers that can distribute PCBs to great distances from the original source point. Although adsorbed PCBs resist migration into the water fraction, PCBs enter the food chain by ingestion and desorption in microorganisms leading to eventual bioaccumulation and biomagnification of PCBs in higher organisms upwards in the food chain (Čonka et al., 2014; Čonka et al., 2015).

Several methods for PCBs degradation in environmental matrixes 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 bioaugmentation and biostimulation (Dercová et al., 2015).Biostimulation is based on encouragement of growth of the indigenous pollutant-degrading microorganisms. Acceleration of the microbial turnover of chemical pollutants generally depends on the supply of carbon, nutrients such as nitrogen (N) and phosphorus (P), on temperature, available oxygen (O_2), soil pH, and the type and concentration of the organic pollutant (Dudášová et al., 2012; Dercová et al., 2015). 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. Bioaugmentation approaches appear to have great potential for remediation of aromatic compounds (Mrozik et al., 2010; Egorova et al., 2013).

The main objective of this study was to evaluate the effect of biostimulation (N, P, O_2) on the growth of biomass and PCB-degradation capability of the indigenous microorganisms in the contaminated sediment taken from the polluted Strážsky canal, as well as to assess the effect of bioaugmentation (re-inoculation of sediment by the bacterial isolates obtained from the sediment) to enhance the biodegradation of PCBs and of a combination of bioaugmentation and biostimulation (inoculation and enhancement of PCB solubility using addition of surfactants).

2. MATERIALS AND METHODS

2.1. Bacterial strains

Bacterial strains with PCB-degradation ability (*Achromobacter xylosoxidans, Rhodococcus* sp., *Starkeya novella, Stenotrophomonas maltophilia*) were isolated as described in our previous study (Dudášová et al., 2014) from PCB-contaminated sediment by selection pressure of PCBs (commercial mixture of PCBs Delor 103 at the final concentration of 100 mg.l^{-1}) and biphenyl (the final concentration of 2.5 g.l^{-1}). Bph gene encoding biphenyldioxygenase was detected previously in chromosomal and plasmid DNA only in *A. xylosoxidans*. Colony counting during biodegradation: One ml of medium was diluted in sterile PCA medium and applied to Petri dishes. After 48 h 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 Biostimulation technique

Biostimulation was performed in 250/500 ml Erlenmeyer flasks closed with a cotton wool stopper. Twenty g of dried non-sterile sediment was mixed with 100 ml mineral medium. Two different experimental patterns were set up. The first set of experiments was carried out with sediment mixed with mineral medium containing additional nitrogen (N) and phosphorus (P) sources (500 mg.kg^{-1} $NaNO_3$ and 1800 mg.kg^{-1} Na_2HPO_4). The second set used sediment mixed with mineral medium with additional nitrogen, phosphorus, and oxygen sources (500 mg.kg^{-1} $NaNO_3$ and 1800 mg.kg^{-1} Na_2HPO_4, increased oxygen concentration was provided by using a flask of bigger volume – 500 ml). Untreated sediment mixed with the mineral medium was used as the control. All flasks were incubated at 28 °C on a rotary shaker (180 rpm) for 21 days in the dark.

2.3 Bioaugmentation technique

Bioaugmentation was carried out in 250 ml Erlenmeyer flasks closed with a cotton wool stopper. Twenty g of dried sterile/non-sterile sediment was mixed with 100 ml mineral medium. Three selected bacterial strains isolated from sediment sampled from Strážsky canal and eight consortia were selected and constructed for bioaugmention of sterile sediment contaminated with PCBs. 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 consortium of two degraders was used, concentration of the added suspension of each strain was 0.5 g.l^{-1}, while in the case when consortium consisted of three degrader suspension of each strain was used in concentration of 0.33 g.l^{-1}. Concentrations of biomass were evaluated according to the absorption and calibration curves. Sediment mixed with the mineral medium free of biomass was used as control. The flasks were incubated at 28 °C in stationary position for 21 days in the dark.

2.3.1 Bioaugmentation and biostimulation technique

The biodegradation set of experiments was carried out in the sterile 250 ml Erlenmeyer flasks. Bioaugmentation of sediment using bacterial strain *S. maltophilia* was stimulated by two synthetic surfactants Triton X and Tween 80. Triton X was used within each of three parallels at the concentration 0.3% w/w which is twice the value of its critical micelle concentration (CMC). Tween 80 was also used within each of three parallels at the concentration 0.032% w/w which is twice the value of its CMC. Amount of dried non-sterile sediment, mineral medium, biomass concentration, and control remained the same as described above.

2.4 PCB extraction and analysis

After the 21 days of degradation 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 and analyzed by GC. Internal standard PCB 209 was used for determination of the extraction efficiency, with recovery of 85.3 %.

All determined PCB congeners were analyzed by gas chromatography (GC) using an Agilent 7890A device 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), a column temperature program: initial temperature 70 °C (2 min) to 150 °C at 25 °C.min^{-1} (0 min), from 150 °C to 200 °C at 3 °C.min^{-1} (0 min), from 200 °C to 280 °C at 8 °C.min−1 (3 min); carrier gas: H2 (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 N2 40 ml.min^{-1}. Identification of seven PCB congeners (28, 52, 101, 118, 138, 153, and 180) 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 PCB congeners was used for calibration.

2.5 Data analysis

SPSS (version 22) and Microsoft Excel were used for statistical evaluation (Kruskal-Wallis One Way Analysis of Variance on Ranks). Level of $p < 0.05$ was considered statistically significant. The extent of degradation was calculated from the mean values and expressed as percentage. Concentrations of all observed PCB congeners were above detection limit. All experiments were performed in triplicate. The amount of eliminated PCBs was evaluated according to the equation: $X= (M_i- M_a)/Mi * 100\%$, where X stands for the biodegradation of the individual PCB congeners in the specific system (%), M_a is the total amount of individual PCB congeners determined in the system after 21 days of cultivation (μg), and M_i is the initial amount of the individual PCB congeners (μg). Final result also considered the amount of evaporated PCBs during the experiment, which never exceeded 5 % of the initial amount of PCBs present in sediment.

3. RESULTS

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 mixture DELOR 103 that in total produced approximately 21 500 tons of this product (Dercová et al., 2008). 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. Contaminated sediment was chosen for aerobic degradation using biostimulation of an indigenous microbial consortium and bioaugmentation performed by inoculation of sediment by isolated bacterial strains able to degrade PCBs from the same sediment. To ensure successful biodegradation, the microorganisms must be present that possess required genes encoding biphenyldioxygenase responsible for start of the particular degradation metabolic pathway. In our previous study (Dudášová et al., 2014),*bphA* gene (chromosomal DNA) was detected only in the *Achromobacter xylosoxidans*, however all other used strains also enhanced degradation of PCBs at certain levels, even though the *bphA* gene was not detected on chromosomal DNA. Considering these facts we assume that gene or cluster of genes coding enzymes responsible for degradation activity is located probably on plasmid DNA.

3.1 Biostimulation technique

The biostimulation process depends on the metabolic potential of the indigenous microorganisms to detoxify or transform the pollutant molecule, which is dependent mainly on its bioavailability. Although 11 bacterial strains we isolated and identified in the contaminated sediment, other cultivable and non-cultivable strains are probably also involved in biodegradation. Although autochthonous microflora with potential for remediation is present in sediment, there are several factors that could inhibit degradation of pollutants e.g. low nitrogen or phosphorus availability, absence of electron acceptors or donors or lack of enzymatic inducers. Therefore, we have used two sets of different cultivation conditions to monitor influence of biostimulation on PCBs degradation using additional nitrogen and phosphorus sources in the first set and additional nitrogen, phosphorus and oxygen sources in the second set. The number of CFUs of the indigenous microorganisms were determined at the beginning (1^{st} day) and at the end of experiment (21^{st} day). The estimated initial CFUs number of natural microflora was in the range 1×10^8 - 5×10^8. At the end of the biostimulation experiments, we observed significant increase of CFU number to 64×10^8 (in a set using 500 ml flask due to addition of oxygen) and 53×10^8 (in a set using 250 ml flask). Such result was expected since macronutrients such as N and P are one of the most important components responsible for bacterial growth. These results also imply that concentration of oxygen is a very important factor influencing CFUs number. Degradation of PCBs using natural microflora stimulated by addition of N and P was significantly higher than degradation without the addition of utilizable source of phosphorus and nitrogen. It is also noteworthy, that removal of PCBs was more effective in an experimental set using 500 ml flasks (increased O_2 concentration) and increased amount of N and P ($p < 0.05$). Higher PCB removal in an experiment using addition of nutrients and oxygen compared to those without addition of O_2, was expected since the enzymes responsible for cleavage of aromatic rings are dioxygenases that need molecule of oxygen as a substrate. The most degraded congener was almost in all cases PCB 28, which can be explained by its best bioavaibility (91 %) in this specific system. Using biostimulation process eliminates a number of steps such as isolation, identification, preservation, cultivation of microorganisms and transporting inoculum to the contaminated location that make bioaugmentation more demanding in comparison to biostimulation. However, biostimulation is conditioned by the presence of the sufficient number of indigenous microorganisms at contaminated sites.

3.2 Bioaugmentation technique

Bioaugmentation using the single bacterial strain

Three bacterial strains isolated from long term contaminated areas were individually used in separate experimental settings. The high degradation capability of single strain in sterile sediment was detected in all bacterial strains in the following order: *Rhodococcus* sp. (87%), *S. maltophilia* (64%), *A. xylosoxidans* (32%).Bacterial strain *Rhodococcus* sp. had the highest potential to eliminate PCB congeners and was able to increase number of CFUs during 21 days of degradation. Biomass of *A. xylosoxidans* expressed in CFUs remained almost at the same level, while biomass of *S. maltophilia* decreased.

A similar experiment under the consistent conditions using single bacterial strains *Rhodococcus* sp., *A.xylosoxidans* and *S. maltophilia* was performed with non-sterile sediment to determine degradation potential of single strain influenced with autochthonous microorganisms present in sediment. Total degradation of seven PCB congeners decreased for *Rhodococcus* sp. (70%), for *A.xylosoxidans* (30%), and for *S. maltophilia* (60%). The decreased PCB elimination might be caused by several factors such as competition of substrates and nutrition between the indigenous and the exogenous bacteria, cross enzyme inhibition or predation.

Bioaugmentation using bacterial consortia

Efficient biodegradation of a broad range of pollutants using consortia constructed from several autochthonous microorganisms has proven to be successful strategy for environmental decontamination. In this study we investigated degradation potential of eight bacterial consortia. Although elimination of PCBs by each consortium containing strain *Rhodococcus* sp. was not below 60%, only two consortia *Rhodococcus* sp. + *Starkyea novella* (68%) and *Rhodococcus* sp. + *Starkyea novella* + *A. xylosoxidans* (79%) were able to increase biomass during 21 days. Moreover, these two combinations of selected bacterial strains were able to eliminate the highest number of seven PCB congeners among all studied consortia. High degradation potential of a consortium made of *Rhodococcus* sp., *S. novella* and *A. xylosoxidans* can be explained by synergistic effect of all used microorganisms. Based on this finding, we assume that *Rhodococcus* sp. has several valuable properties including efficient degradation capacity and sufficient survival capability in consortia of microorganisms.

The lowest degradation was observed in the consortium consisting of *S. maltophilia* and *Stenotrophomonas* sp. which eliminated less than 10% of the initial amount of PCBs. In this consortium, significant decrease of CFUs by 57.5% was observed. It can be explained by the presence of antagonistic effects caused most likely by a competition of those two strains for nutrients. Decrease of biomass and low removal of PCBs could be also caused by a competition for substrate and cross-inhibitory effect of different enzymes. The most degraded congeners were PCB 28 and PCB101, whereas the lowest degradation was observed for PCB 52 and PCB 180. Therefore, it can be concluded that low biodegradation of less chlorinated PCBs such as PCB 52 and PCB 118 can result from the fact that more chlorinated PCB congeners were probably dechlorinated to lower chlorinated biphenyls.

Bioaugmentation combined with the biostimulation

The following experiment was carried out to evaluate the effects of two synthetic surfactants (Tween 80 and Triton X applied separately) on PCB removal in the presence of bacterial strain *S. maltophilia*. In both experiments, toxic effects of used surfactants on the microbial growth and activity were not observed. Bioaugmentation using strain *S. maltophilia* without added surfactant showed a slight decrease of CFU number by 7.5×10^8. In the experiment using *S. maltophilia* with application of the non-ionic surfactant Tween 80, the biomass revealed increased CFU number by 272×10^8. When the second non-ionic surfactant Triton X was used, CFU increased by 247×10^8. In both cases of the addition of synthetic surfactants, higher biodegradation of PCB congeners ($p < 0.05$) has been documented. The most significant increase in elimination of the seven PCB congeners was observed with the use of synthetic surfactant Tween 80. When compared to a similar set without the addition of Tween 80, biodegradation was increased about 19 %. Addition of surfactant Triton X increased PCBs removal by 7 % compared to the control bioaugmentation experiment using inoculation of the same bacteria in the absence of surfactant.

4. CONCLUSIONS

Based on the results mentioned above, it can be concluded that both biostimulation and bioaugmentation render promising results and lead to a successful bioremediation of sediments under laboratory conditions. The most successful bioaugmentation approach seems to be the use of a bacterial strain *Rhodococcus* sp. Despite the high degradation potential of this strain, its application in real *in situ* process would require considerable energy and time consumption due to the preparation of the inoculum. Other approaches that showed relatively effective degradation were bioaugmentation using bacterial consortium *Rhodococcus* sp., *Starkeya novella*, and *Achromobacterxylosoxidans*. 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). Biostimulation of natural microflora by increased amount of oxygen and utilizable source of nitrogen, phosphorus, or surfactants has shown to be comparable with bioaugmentation in the terms of degradation efficiency. The effectivity of both used techniques depended on the initially present or inoculated bacteria, their amount and viability. Ecotoxicity of sediments after the biotreatment 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 polluted sites contaminated with PCBs.

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ELIMINATION AND TOXIC EFFECTS OF POLYCHLORINATED BIPHENYLS IN REAL CONTAMINATED SEDIMENT

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KEYWORDS
Bioaugmentation, Biostimulation, PCBs, Sediment, Terpenes

INTRODUCTION

Polychlorinated biphenyls (PCBs) are substantial biphenyl derivatives with 1-10 atoms of chlorine. They were synthetized from 1959 until their production was banned and stopped in 1984 in Slovakia. The production caused enormous problems in health of people who worked in the factory and as well as in the environment in whole Michalovce District. Bioaugmentation, a process when microorganisms are inoculated into contaminated sediment with the aim to enhance degradation of PCBs, was performed in microcosms using bacterial isolates with PCB-degradation ability obtained from the contaminated sediment *Achromobacter xylosoxidans*, *Stenotrophomonas maltophilia* (Dudášová et al., 2014), and *Pseudomonas stutzeri* (Dercová et al., 2008), an isolate from soil contaminated with PCBs from the vicinity of the former PCB producer. Biostimulation of growth and degradation ability of indigenous microflora was performed using addition of cutted plants with terpenes content (ivy leaves and pine needles) known PCB degradation inducers (Hernandéz et al., 1997). Ecotoxicity of contaminated sediments was evaluated using biotests of the standard aquatic plant *Lemna minor*.

MATERIAL AND METHOD

Sediment contaminated with PCBs from Strážsky canal was sampled using Uwitec sampler (AT) at the place with N 48°51.42,3” E 21°50.24.4” (Garmin GPSmap 76). Chemical properties of sampled sediment: total organic carbon (TOC) 21.9 $g.kg^{-1}$, pH 6.94 - 7.24, redox potential -197-439 mV, dry weight 20 - 63%, organic matter 1.05 - 7.06%, and PCB congeners present in the sediment are from the commercial mixture Delor 103. Delor 103 is a mixture that was produced in Chemko Strážske a.s. during years 1959 - 1984.

Bacterial strains *Achromobacter xylosoxidans* and *Stenotrophomonas maltophilia* isolated from contaminated sediment and strain *Pseudomonas stutzeri* isolated from soil in the vicinity of the factory were used. For bioaugmentation method bacterial strains were cultivated in Broth medium No. 2 (Immuna, SR) for 48 h and added to the sediment (1 $g.l^{-1}$). Minimal mineral (MM) medium was prepared according to Dudášová et al. (2014), 100 ml of MM medium was addedinto each flask with 20 g of contaminated sediment. For biostimulation plants with terpene content (ivy leaves, pine needles), which according to Hernandéz et al. (1997) induce enzyme biphenyldioxygenase (enzyme responsible for the first step in PCB degradation), were added to the contaminated sediment (0.75 g). Experiments were carried out under the following conditions: 21 day cultivation in the dark at 28°C with irregular mixing.

Ecotoxicity test was performed using standard plant *Lemna minor* (10 leaves (fronds)) for 7 day-incubation with 10 g of remediated sediment, 90 ml of Steinberg medium and inhibition parameters: Ir1 - the growth rate for number of fronds, Ir2 – the growth of biomass for number of fronds, Ia1- the growth rate for area of fronds, Ia2 – the growth of biomass for area of fronds, were evaluated according to ISO 20079 (2008).

RESULTS AND DISCUSSION

This paper deals with monitoring of added microorganisms degradation effect (bioaugmentation), inducer addition (biostimulation) and combination of these two methods. Our results indicate that native microorganisms present in sediment and the enrichment with bacterial strains (bioaugmentation) isolated from the same contaminated sediment are better degraders of PCB congeners than the strain isolated from PCB-contaminated soil, *P. stutzeri* shown in Fig. 1. Amounts of the individual PCB congeners estimated during the biodegradation of PCBs in the presence of *Achromobacter xylosoxidans, Stenotrophomonas maltophilia*,and *Pseudomonas stutzeri*combined with an addition of ivy leaves and pine needles arepresented in Fig. 1. As it can be seen, the most abundant PCB congeners at the beginning of the treatment were the PCB congeners 28 (tri-CB) and 52 (tetra-CB). The most significant decrease throughout the biodegradation was observed for the lower chlorinated PCB congener 28.

S. maltophilia increased degradation of six indicator PCB congeners in comparison with *A. xylosoxidans* and *P. stutzeri.* The addition of ivy leaves increased the toxic effect of the sediment bioaugmented with *P. stutzeri* on *L. minor* while pine needles had no effect on the toxicity of the sediment (Fig. 2). *A. xylosoxidans* did not show such biodegradation effect on PCBs as *S. maltophilia*; but, on the other hand, sediment bioaugmented with *A. xylosoxidans* had no toxic effect on the *L. minor* while that bioaugmented with *S. maltophilia* had toxic effect on the used bioindicator. Pine needles increased the toxicity of sediment augmented with *A. xylosoxidans* and decreased the degradation effect, as well as the toxicity of the sediment bioaugmented with *S. maltophilia*.

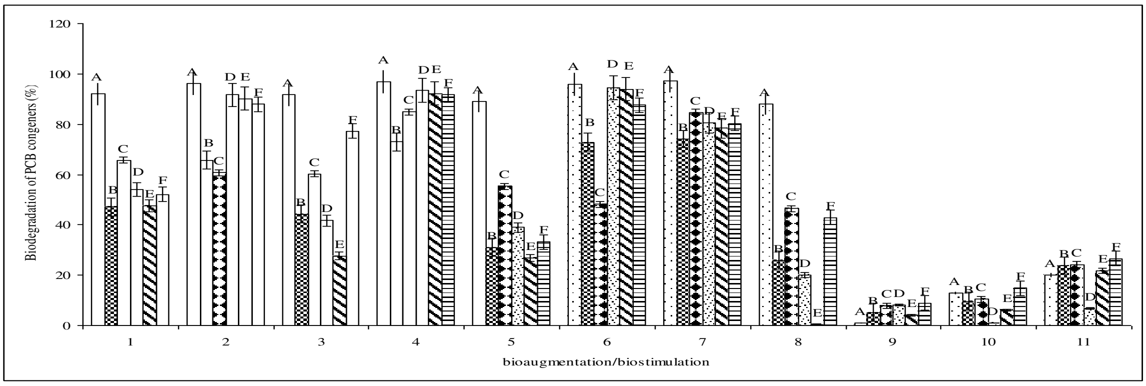

Fig. 1. Biodegradation of six indicator PCB congeners in contaminated sediment from Strážsky canal using bioaugmentation (microorganisms) and/or biostimulation (plant material with terpenes): 1 – *A. xylosoxidans*, 2 – *S. maltophilia*, 3 – *A. xylosoxidans* + ivy leaves, 4 – *S. maltophilia* + ivy leaves, 5 – *A. xylosoxidans* + pine needles, 6 – *S. maltophilia* + pine needles, 7 – ivy leaves, 8 – pine needles, 9 – *P. stutzeri*, 10 – *P. stutzeri* + ivy leaves, 11 – *P. stutzeri* + pine needles.; A – PCB 28, B – PCB 52, C – PCB 101, D – PCB 118, E – PCB 138, F – PCB 153.

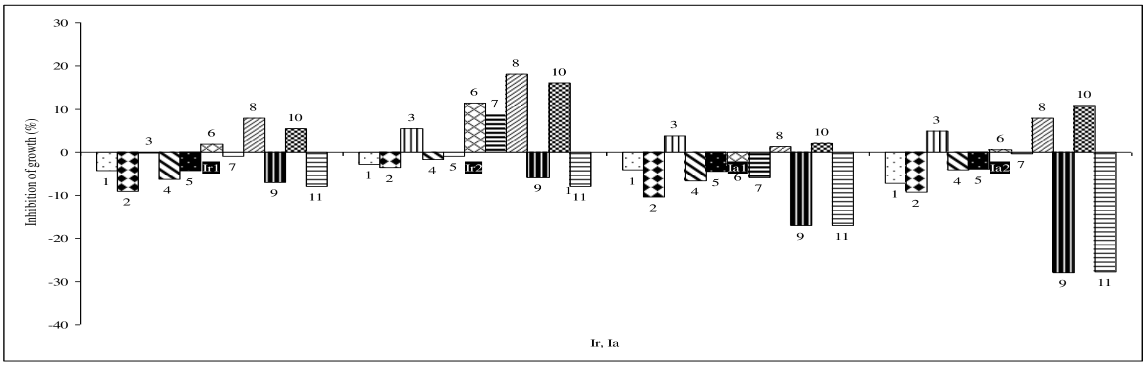

Fig. 2. Ecotoxicity of sediment after bioremediation measured using plant indicator*Lemna minor*: *A. xylosoxidans*, 2 – *S. maltophilia*, 3 – *A. xylosoxidans* + ivy leaves, 4 – *S. maltophilia* + ivy leaves, 5 – *A. xylosoxidans* + pine needles, 6 – *S. maltophilia* + pine needles, 7 – ivy leaves, 8 – pine needles, 9 – *P. stutzeri*, 10 – *P. stutzeri* + ivy leaves, 11 – *P. stutzeri* + pine needles.

CONCLUSION

Our results show that the most suitable biotreatment for PCB degradation enhancement is the biostimulation of the contaminated sediment using ivy leaves as potential PCB degradation inducer and bioaugmentation using bacterial isolates from the contaminated sediment. The obtained results can be useful for the proposal of bioremediation technologies on PCB-contaminated sites, mainly aquatic sediments.

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INTEGRATION OF THE PUBLIC INTO THE CONTAMINATED SITES REMEDIATION

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KEYWORDS
Project, awareness, education of the public, publications

The project **Integration of the public into the contaminated sites remediation**is a further project undertaken by the Slovak Environment Agency which is aimed at promoting and raising public awareness of contaminated sites in Slovakia. It is directly related to the project *Awareness:Working with the Public to Facilitate the Handling of Environmental Contamination in Slovakia (09/2014–08/2015),* which is supported in the same way – from the Environment Operational Programme.

The need to involve the general public in addressing issues of environmental contamination stems from the results of previously implemented projects by the agency: *Systematic Identification of Contaminated Sites in the Slovak Republic (2006-2008), Regional Studies of the Environmental Impacts of the Contaminated Sites in Selected Regions (2008-2010)* and *Completing of the Environmental Contamination Information System (2009-2014).*

The project is aimed at target groups which consist of competent individuals in the field of environmental contamination, specialists from the field of environmental education and training, nursery, primary and secondary school teachers as well as university lecturers, students and researchers. Numerous activities in the project focusing on the topic of environmental contamination will be taking place from 2014-2015, such as international conferences, various specialised courses, tuition of teachers, issuing of publications on environmental contamination, etc.

Main project activities:

- to hold an international conference aimed at environmental contamination issues 2015,
- publication for the International Conference 2015,
- specialised course –Risk analysis of polluted areas (3x3 days),
- exercises –Risk analysis of polluted areas,
- training Course for university lecturers and doctoral postgraduate students (1x3 days),
- publication – monograph on environmental contamination,
- lecture/field Course on surveying and remediation methods of environmental contamination (1x5 days),
- translation of legal regulations and specialised documentation, information system of EC,
- environmental Contamination training course for teachers (primary and secondary) (10x1 day)

Basic information on the project to involve the public in addressing environmental contamination:

Priority axis:	4 Waste Management
Operational objective:	4.4 Addressing issues of environmental contamination including their removal
Source of finance:	Cohesion Fund within the Environment Operational Programme
Implementation period:	9/2014 – 8/2015
Main objective:	Involvement of the general public and promotion of activities concerning environmental contamination and its remediation
Project leader:	Ing. Zuzana Ďuriančíková
Webpage:	http://www.sazp.sk/public/index/go.php?id=397&idl=397&idf=1061&lang=sk

MANAGEMENT OF SITES CONTAINING POPS MIXTURES OR PESTICIDES IN THE SLOVAK REPUBLIC

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KEYWORDS
POPs (persistent organic pollutants), obsolete pesticides, pesticide stores, monitoring

Under the auspices of the Operational Programme Environment, the Slovak Environment Agency is undertaking the **Management of sites containing POPs mixtures or pesticides** project as part of the Slovak Republic's commitment to the Stockholm Convention and EU and Slovak legislation. Under this convention, almost 200 countries from around the world committed themselves to taking measures to reduce the adverse effects on public health and the environment deriving from POPs. This concerns the restriction, or total ban of production and use, of more than 20 types of chemicals, especially pesticides, but also including industrial substances and the unintentionally produced POPs. DDT represents the well known substance among pesticides , however, stocks of other chemicals, such as Toxaphene and Endosulfan were found found in Slovakia. Regarding industrial chemicals, considerable problems are presented by polychlorinated biphenyls (PCBs) in Slovakia which were produced at Chemko in Strážske for decades. They were used as a component of electrical equipment in high volumes.

The synthesis of the first materials, known as POPs began over 130 years ago (pesticide DDT in 1874). The discovery of their effectiveness on living organisms, labelled then as "damaging insects", brought with it the Nobel Prize for Swiss chemist P. H. Müller in 1948. Further POPs were produced in subsequent years and applied in huge quantities in the USA and Europe.

Relatively soon after the massive application of POPs, strong pressure appeared condemning the production and use due to significant environmental and health risks. These derive from their physicochemical properties which meant that they were useful in various areas. Namely, their high stability or low degradability which should have ensured a 'competitive advantage' over other chemicals due to their long life. This apparent advantage, however, proved to be the opposite, as any release into the environment or into the cells of living organisms meant minimal break down of the material and this presented long term risks. In particular, in terms of primary biological activity - the acute and chronic toxicity and other effects for which POPs were initially developed and manufactured (as pesticides). Due to this combination of mentioned characteristics (toxicity together with low degradability) a wave of opposition to the use of POPs emerged built upon the evidence of ecologists, biochemists and other scientists concerning the bioaccumulation of POPs in organisms and the environment. As a typical example is the high concentrations of DDT discovered in the bodies of birds of prey (at the top of the food chain) and given as the reasons for damage to their reproductive organs and consequent drop in their populations. Negative calls on the application of POPs resulted in the adoption of the Stockholm Convention and further legislative acts at national and international levels.

The project is aimed, above all, at the stocks of obsolete POP pesticides which exist in Slovakia – inherited from a time when their application was allowed. Thanks to the previous activities by the Slovak Environmental Agency, for example, the project of Systematic Identification of Environmental Contamination, there are approximately 50 such warehouses or stores registered on the Environmental Contamination Information System (ECIS). A project team undertakes field surveys to update existing data on warehouses and the storage of agrochemical types and amounts. POPs are identified according to their commercial names and an approximate estimation of quantities stored is made. Analogous investigation is performed inwarehouses thatcomply with the requirements of the Central and Testing Agricultural Institute, to ascertain whether stocks of obsolete POPs pesticides may be found in these warehouses.

Selected stores, which likely represent a great risk to the environment, will feature in detailed geological surveys of the environment. These stores were identified, as a part of preliminary assessments on the basis of environmental contamination classification, from the viewpoint of pollution spread risk into groundwater (i.e. high permeability of subsoil and ground water level just below ground level). Samples are taken from bedrock, groundwater and building materials in order for laboratory analysis to determine contaminant concentration. If, on the basis of the survey, pollution is confirmed in amounts exceeding limit values, the preliminary risk assessment is updated (classification of environmental contamination) and the location is transferred from ECIS section A (likely environmental contamination) to section B of the register (confirmed environmental contamination). On the basis of the environmental contamination classification, it is then recommended which of these stores should be considered as priority for treatment. Subsequent detailed geological surveys of the environment, a part of which is risk analysis of the polluted area, provide proposals for priority remediation (remediation works, however, are not a topic in this project.

Serious problems in the Slovak Republic are not only presented by stocks of obsolete pesticides, but also by the presence of PCBs in electrical equipment and widespread contamination in the Zemplín area. Waste water, which hadn't been sufficiently treated at the Chemko plant in Strážske, flowed out via the Laborec river into the Zemplínska Šírava reservoir. Numerous studies have confirmed an alarming level of environmental contamination in the affected area, but also elevated PCB levels and their metabolites in the blood serum of the population.

Technological proposals will be made at the end of the project to assess the actual possibilities to environmentally friendly and safely disposal of the POPs wastes. Estimation of the financial resources necessary to address these individual issues will form a separate chapter of the study. .

Project will be terminated on June 30th 2015.

PRELIMINARY EVALUATION OF GROUND WATER QUALITY IN THE SURROUNDING OF LEACH RESIDUE PILE NEAR SEREĎ CITY (SLOVAKIA)

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KEYWORDS

Leach residue pile, Sereď city, Ni-Fe ore treatment, groundwater contamination

ABSTRACT

On behalf of the Ministry of Environment of the Slovak Republic was called a state project entitled as “Monitoring of environmental loads for the chosen sites in the Slovak Republic”. The goal of this project was to make a proposal of and to build a monitoring network, made by monitoring boreholes used mainly for ground water quality evaluation. There were around 160 sites selected for monitoring of ground waters, where one of those sites is leach residue pile near Sereď city in Slovakia, where the Fe-Ni ore treatment was performed during the years 1963 – 1993. Leach residue is an untreated ore together with extracting chemicals, which was piled up to the present size coming to 6,5 millions of tons.

The area consists mainly of gravels, graveolous sands and sands with high permeability, which overlay neogeonic bedrock. The main source of ground waters is river Váh, flowing northerly from the source of potential contamination. Thus, a conceptual model was made on the assumption of contamination plume spreading in the general direction of underground waters flow (south to south east). Monitoring boreholes were situated south from the leach residue pile as shown in figure 1.

Fig. 1. Ground water monitoring net (red labels) in the surrounding of leach residue pile; southeastern view at the denuded part of leach residue pile (on the right)

In the past were leachates from the leach residue pile percolating into the ground waters, which was considered as the main process of contamination of ground waters in the surrounding of leach residue pile. The high values of ammonium, nitrates and sulphates were found (Klaučo et al., 1994, Polák, 2000). Klaučo et al. (1994) predicted the main spreading plume of ammonium, nitrates and sulphates. Nowadays, preliminary observations showed similar results of higher values of these compounds, especially ammonium, chlorides, nitrates and sulphates (table 1). Ground water pH and electric conductivity (in situ measuring) varies between 6,9 – 7,9 and 120 – 250 mS.m^{-1} respectively. We found an evidence of high amounts of nickel among the potential toxic trace metals in ground waters close to (up to 10 meters away) leach residue pile, while no content of nickel was found in samples taken from farther monitoring boreholes (more than 50 meters). Higher contents of other potential toxic trace elements were not confirmed.

Tab. 1. Contents of selected parametersin ground waters close to and below (in the meaning of general ground waters flow) leach residue pile (in mg.l^{-1})

Object	Date	NH_4	Cl	NO_3	SO_4	HCO_3	Na	Ni
VN24-2	06.11.2014	5,6	64,2	117	166	523,4	48,2	-2
VN24-4	06.11.2014	9,95	55,4	-1	55,9	940,6	57,2	10,5
VN24-5	06.11.2014	8,4	70,1	137	175	495,3	50,6	-2
VR24-2	12.11.2013	28,6	56,7	3,3	681	914,4	195	320
VR24-2	06.11.2014	19,5	55,1	-1	941	922,3	384	739
VR24-4	12.11.2013	42,5	55,4	8,4	103	792,4	40,1	32
VR24-4	06.11.2014	7,9	54,2	-1	70	950,4	63,1	523,9
VR24-5	06.11.2014	0,1	82,5	127	265	379,4	33,4	-2
VR24-5	14.11.2013	0,05	196	120	432	495,3	38,3	-2

Monitoring of ground waters could help to distinguish between other sources of potential contamination especially industry and agriculture, which are intensively exploited in this area.

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APPLICATION OF HYPOCHLORITE SOLUTIONS IN REMEDIATION OF SURFACES CONTAMINATED BY BLISTER CHEMICAL AGENTS

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KEYWORDS
Decontamination, blister agent, hypochlorite solutions, emulsion

ABSTRACT

This paper presents the basic mechanisms for the chemical decontamination and comparative results of testing efficiency of the different decontamination materials in case of chemical contamination with mustard gas $S(C_2H_4Cl)_2$, poison from a group of blister chemical agents. Experimental setup in this study comprises application of S-mustard on two different samples: metal plate colored alkyd-carbamide and rubber sample based on natural caoutchouc. As a decon solutions was used water solution of $Ca(OCl)_2$ with different percentages of active chlorine and two types of emulsions containing tetrachloroethylene and emulsifiers PV-6 and PV-10. It was concluded that degradation rate of S-mustard grows with increasing content of active chlorine ("ACh") in the decontamination solutions. Tests results indicate the rubber surface can be successfully decontaminated by using an emulsion with tetrachloroethylene and FN-10. Also, efficacy of decontamination increases rapidly if decon solution is heated (48 °C).

CHEMICAL DECONTAMINATION

Chemical decontamination aims to removed highly toxic substances (HTC) from the surface, air, water or other environments, in the shortest possible time. Within the decontamination procedure, one or more methods of decontamination can be applied, while decontamination procedures could be based on chemical, physical or mechanical processes (Martens & Gorgens1992). The solutions based on alkaline metal hypochlorites has been used a long time for decontamination of the facilities and objects contaminated with HTCs or biological agents, as well as for the drinking water disinfection. Hypochlorite solutions in water are very effective against most of HTCs and were still irreplaceable in final decontamination, despite some significant disadvantages (Franke Töpferm 2001, Trapp 1985, Yang, Baker & Ward 1963).

In most cases today, for HTCs decontamination is using calcium-hypochlorite $Ca(OCl)_2$, whose water solution gives alkaline reaction, and poly-decontamination activity is based on the "active" chlorine content (chlorine in $^{+}1$ electronic form, two electrons missing to achieve a stable configuration). Martens & Gorgens(1992) explained thatin $Ca(OCl)_2$ water solutions occurs more active components, whose ratio depends on the pH of the environment (Fig. 1).

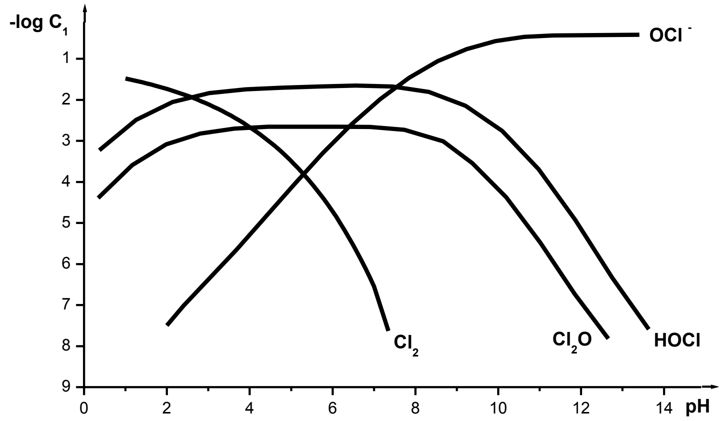

Fig. 1. The content of active components in the $Ca(OCl)_2$ water solutions depending on the pH values

EXPERIMENTAL RESULTS

In order to check decontamination effectiveness, authors have tested efficacy of several decon solutions on the samples contaminated by blister chemical agent - sulfur mustard. Contamination by sulfur mustard was performed on metal plates, colored with alkyd-carba-midnite smear layer, and rubber-coated sample based on natural rubber.

Tab. 1. Comparative efficacy of different formulations based on hypochlorite solutions against the S-mustards

N°	Decon solution	S-mustard desorption 60 min after decontamination	
		alkyd-carbamide coating	rubber based on natural rubber
1.	$Ca(OCl)_2$ water solution with 0.5 % "ACh" (active chlorine)	0,143± 0,074	0,83± 0,20
2.	$Ca(OCl)_2$ water solution with 1.1 % "ACh"	0,041± 0,037	0,76± 0,09
4.	$Ca(OCl)_2$ water solution with 5.0 % "ACh"	0,009± 0,002	0,52± 0,023
5.	$Ca(OCl)_2$ water solution with 2.0 % "ACh" and 0.5% FN-6	0,046± 0,024	1,50± 0,19
6.	$Ca(OCl)_2$ water solution with 2.0 % "ACh" and 0.5% FN-10	0,070± 0,025	0,89± 0,081
7.	Emulsion 1: $Ca(OCl)_2$ water solution with 2.0% "ACh" and 0.5 % FN-6, 99%; diesel-fuel D2, 1%	0,034± 0,015	1,15± 0,50
8.	Emulsion 2: $Ca(OCl)_2$ water solution with 2.0% "ACh" and 0.5 % FN-10, 99%; tetrachloroethylene, 1%	0,038± 0,036	0,445± 0,037

Although chemical reaction conducted in heterogeneous conditions, it is obvious that degradation rate of S-mustard increased with increasing content of active chlorine ("ACh") in the decontamination solutions.Emulsion contains tetrachloroethylene(as an organic phase) and emulsifier FN-10 is effective, especially regarding the decontamination of rubber samples,which are otherwise difficult to decontaminate.Emulsion that consists of diesel fuel (as dispersed organic phase) and emulsifier FN-6, didn’t provide significant results in decontamination of rubber samples (Ceković 2004).In the second study, the effectiveness of decontamination has been observed through the parameter of residual contamination (Δm_s) on the appropriate surfaces.By observing the comparative results for emulsion 2 and different variants of $Ca(OCl)_2$ water solutions, it can be conclude that efficacy of sulfur mustard decontamination was extremely high and ranged from 99.98% in emulsion 2 to up to 99.99% in $Ca(OCl)_2$ water solution with 5.0 % "ACh". The results also showed that emulsion heated on 48 °C can almost completely neutralizes sulfur mustard (with efficiency close to 100%). This high efficiency is explained by the influence of temperature on the $Ca(OCl)_2$ reaction rate with toxic agents in the water phase (Ceković 2004).

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THE WATER QUALITY OF GRAVEL PITS AND THE DANUBE RIVER IN THE URBANIZED AREA OF BRATISLAVA (SLOVAKIA)

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KEYWORDS
Bratislava, Gravel Pits, Danube River, Water Quality, Faecal Contamination, Enterococci

ABSTRACT

The gravel pits water are typical features of Bratislava. They are witnesses of the gravel and sand exploitation of the Danube river alluvial deposits, and are important esthetic and urbanistic features used for public recreation, fishing and swimming. The gravel pits located in the Bratislava region had been mostly formed after World War II due to increasing demand for the gravel-sand material to rebuild the city. By their origin they are related to the river Danube. The water quality is determinated by various indicators, especially hydrochemical and microbiological ones.

The water samples had been taken from 8 gravel pits, and from single location of surface of Danube River. For monitoring were selected three gravel pits on the right hand side of the Danube River (Čunovo, Rusovce and Draždiak), four gravel pits situated on the left hand side of the Danube River (Štrkovec, Kuchajda, Zlaté piesky and Vajnory) and Danube River (Fig. 1).

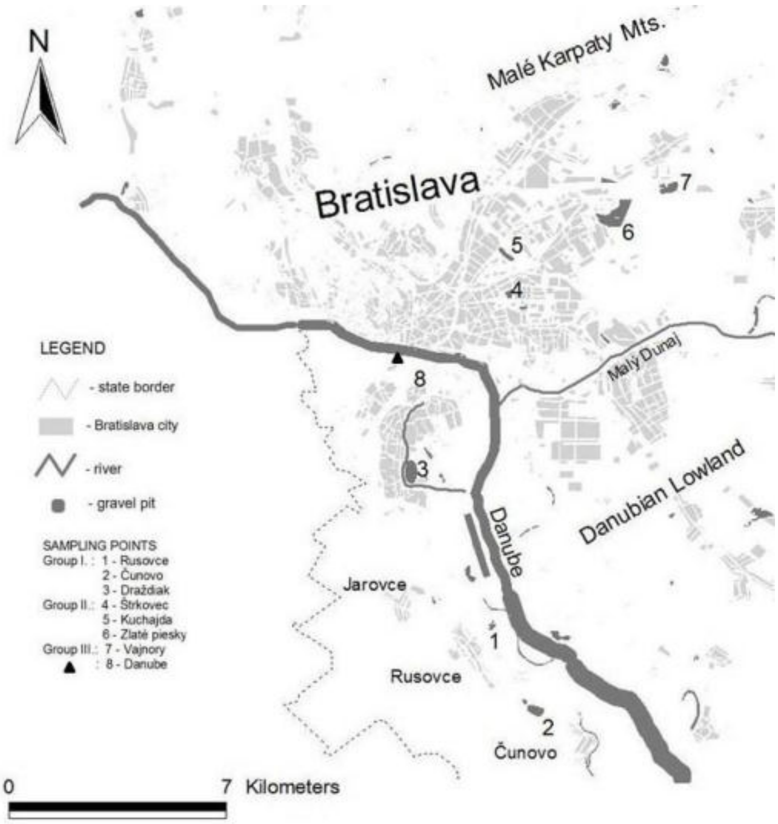

Fig. 1. Sampling sites in the Bratislava area

The chemical composition of the Danube water, as the main source of infiltrated water to the alluvial deposits, has been constant for a long time (Ženišová et al., 2005) and the little changes in it are related to the seasonal minimum and maximum flows (Ženišová et al., 2010). During the infiltration of water from Danube River, its chemical composition is changing, not only with contacts of sediments but specially effect of secondary factors, as are escape form city´s canalization, waste deposits, pollution from chemical industry and so on (Ženišová et al., 2000).

There are three groups of the gravel pits according their chemical composition (Fig. 1). The first group is represented by the gravel pits Rusovce and Čunovo, this chemical composition is almost the same as the water in the river Danube, and are characterized by the lowest conductivity (Fig. 2). The second group is represented by the rest of the gravel pits with the exception of gravel pit Vajnory, where the quality of the water is significantly effected by surrounding city area. To compare with the water of the Danube River we would find significantly higher concentration of main ions, and much higher conductivity. The separate position belongs to the gravel pit Vajnory, that has had the highest conductivity, and the highest concentration of sulphate and chloride ions.

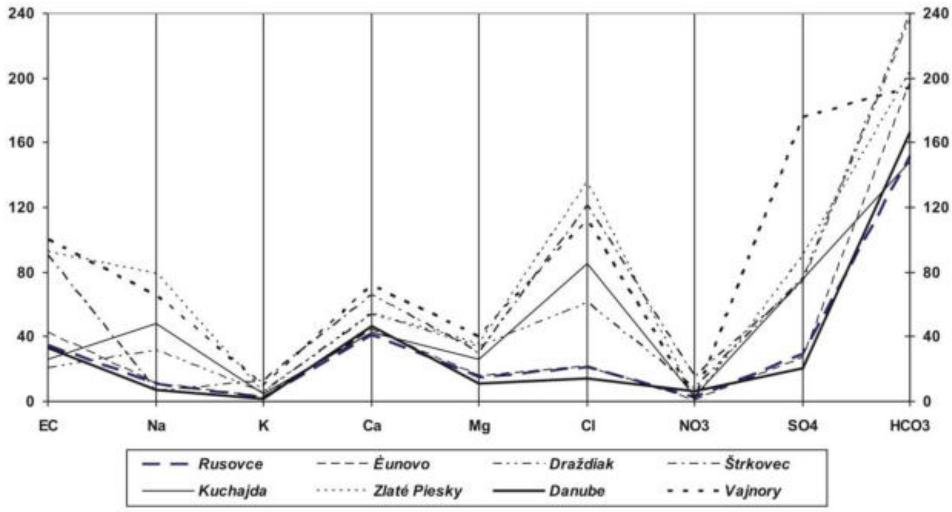

Fig. 2. Water chemical composition of Danube River and gravel pits

In the gravel pits water was determined increase of chlorides concentration and drop of sulphates concentration. Significant indicator of faecal contamination is the presence of enterococci. Faecal enterococci (*E. faecalis*, *E. faecium, E. durans, E. hirae*) dominates in the river Danube, and only two non-faecal enterococcal species, *E. casseliflavus* and *E. seriolicida* was found in the water of gravel pits with other enterococcal very related taxa: *Lactococcus lactis* and *Aeromonas* spp.

The absence of the faecal enterococci in the gravel pits, even during the summer, we can explain by relatively good self-cleaning ability of environment. Low content of nutritious sources expressed as BOD_5, COD_{Mn}, COD_{Cr} and predacious pressure do not create conditions suitable for reproduction of enterococci.The river Danube enters the territory of Bratislava with higher content of enterococci in the samples compared to the gravel pits, what could be explained by higher presence of organic matter in it.

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DECONTAMINATION OF HIGHLY TOXIC CHEMICALS THICKENED FORMULATIONS AT DIFFERENT SURFACES

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KEYWORDS
Contaminant, highly toxic chemicals, thickened agents, chemical decontamination.

ABSTRACT

The highly toxic thickened chemicals are specific formulations of highly toxic chemicals mixed with the substances (usually acrylic resins) in order to increase their durability on contaminated surfaces. The role of thickener is to reduce the volatility of the highly toxic chemicals. Although there are many formulations of thickened highly toxic chemicals (HTC), the most common form of administration is to add an organic polymer, for example, copolymers of methyl-, ethyl-, butyl methacrylate to highly toxic chemicals (S-mustard, soman, VX etc.). This paper presents the results of decontamination of thickened highly toxic chemicals and other specific chemical agents by adsorption materials, alkaline solutions, chlorine-activated materials and micro-emulsions at different surfaces in the environment.

INTRODUCTION

Chemical warfare involves using the toxic properties of chemical substances as weapons. This type of warfare is distinct from nuclear warfare and biological warfare, which together make up the military acronym for nuclear, biological, and chemical (warfare or weapons), all of which are considered "weapons of mass destruction". The first formulation of the thickened HTC were developed in 1930th in Great Britain, when the oxygen mustard gas (O-mustard) was added to sulphur mustard as thickener for use in the form of an aerosol under conditions of hot conditions. Some of the representative's formulation of thickened HTC is:

- irritant, 30-75 % organic solvent (fluororganic derivative), a polymer thickener;
- 92-93 % S-mustard, 2-3 % polymethylmethacrylate, 5 % pyridine, quinoline or picoline;
- thickened lewisite (dynamic viscosity at 25 °C: 0.03 Pa·s;
- 97 % of sarin, 3 % cellulose acetobutyrate;
- VR 55, thickened soman (dynamic viscosity at 25 ° C: 0.175 Pa·s);
- thickened VX (dynamic viscosity at 25 °C: 0.158 Pa·s).

NATURAL DECONTAMINATION OF THICKENED HTC FORMULATIONS

Versatility of contamination carriers and decontamination objects in diversity of conditions and demands, decontamination is very complex scientifically and technical issue and is both time-consuming and demanding in terms of resources. Evaporation of the thickened HTC formulation is carried out in two stages. In the initial stage of the evaporation rate of the thickened soman is no different from ordinary soman. After formation of a thin polymer film on the surface of dispersed droplets, the thickened soman began to decrease the evaporation rate. The value of the diffusion coefficient, which determines the rate of evaporation decreases over time as there is an increase in the thickness of the polymer film.

DECONTAMINATION OF THICKENED HTC FORMULATIONS BY CHLORINATEDDECONTAMINANTS WATER PORRIDGE

Many published results verify the effectiveness of decontamination of ferrous and non-ferrous metal surfaces contaminated with thickened mustard gas or soman, using aqueous slurry super tropical bleach, as follows:

- decontamination of thickened S-mustard by heated solution and special brush - neutralized 100 % of the unpainted metal, metal alkyd primer and painted metal coating, or 95.9 % of the tilt of the initial density of the material contamination;

- decontamination of thickened S-mustard by heated solution, without special brush - neutralized 90.7 %, 98.1 %, 99.4 % and 91.9 % of the initial density of contamination on the unpainted metal, metal alkyd coating, metal colored coating and tarpaulin material, respectively.

DECONTAMINATION OF THICKENED HTC FORMULATIONS BY MICRO-EMULSIONS

To ensure effective decontamination of thickened HTC formulations, micro-emulsion should include two main components: an organic solvent, which is capable of dissolving the polymer and the HTC, and the component and chemically active substance, which is used as a reactant for the actual neutralization of the HTC. Good results in the application of micro-emulsions to the decontamination of thickened HTC formulations are obtained in the decontamination tests of semi-S-mustard, as a model substance for the S-mustard, in mixture with 10 % of polymeric thickener K125. The comparative results of the efficiency of the micro-emulsion in the decontamination of semi-S-mustard, with and without thickeners K125 are presented in the Table 1.

Tab. 1. Comparative efficiency of semi-S-mustard degradation without and in combination with thickeners K125 micro-emulsion

Parameters of the reaction system	**HTC formulations**	
	S-mustard	**semi-S-mustard with 10 % K125**
The degree of degraded HTC, %	97	84
Selectivity of reaction: sulfoxide/sulfone	97 : 3	87 : 13

The present results demonstrate that the micro-emulsions are very suitable for the degradation of thickened HTC formulations, which are thickened by the addition of the polymer.

CONCLUSION

This paper presents the results of decontamination of thickened highly toxic chemicals by adsorption materials, alkaline solutions, chlorine-activated materials and micro-emulsions. Looking forward to the next century, the highest research priority in reactive decontamination is to identify both liquid and solid decontaminants which do not have adverse effects on the environment.

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THE POSSIBILITY OF THE HYBRID POPLAR USE IN THE SOIL PHYTOREMEDIATION PROCESS

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ABSTRACT

Areas being under the impact of industrial plants generally contain in a top soil a high concentration of heavy metals. Very often, utilisation of the area adjacent to the plant is limited to the so-called protective forest, which is designed to reduce the negative impact of the industrial plant to other components of the environment. As an example the Głogów Copper Smelter (Poland) can be used. The protective forest was built based on the poplar clones, *Populus robusta* L. in particular.

For many years in the process of phytoremediation of trace elements from contaminated sites the herbaceous plants have been used. Unfortunately they are characterized by the low biomass. Much better for this process seems to be the trees such as willows and poplar.

The paper presents the results of analysis of concentration of selected heavy metals in the soil and some trees tissues of the Głogów Copper Smelter sanitary zone and the possibility of trees using for elimination of these contaminants from the soil.

Site description

Research points were located in the protective forest of Głogów Copper Smelter (GCS). The site is located in the south-western part of Poland, in Lower Silesia, near the city of Głogów. The study was conducted at the point located approximately 1 km to the north-east (B) and around 100 and 300 m on the south-west (Z1, Z2), Figure 1.

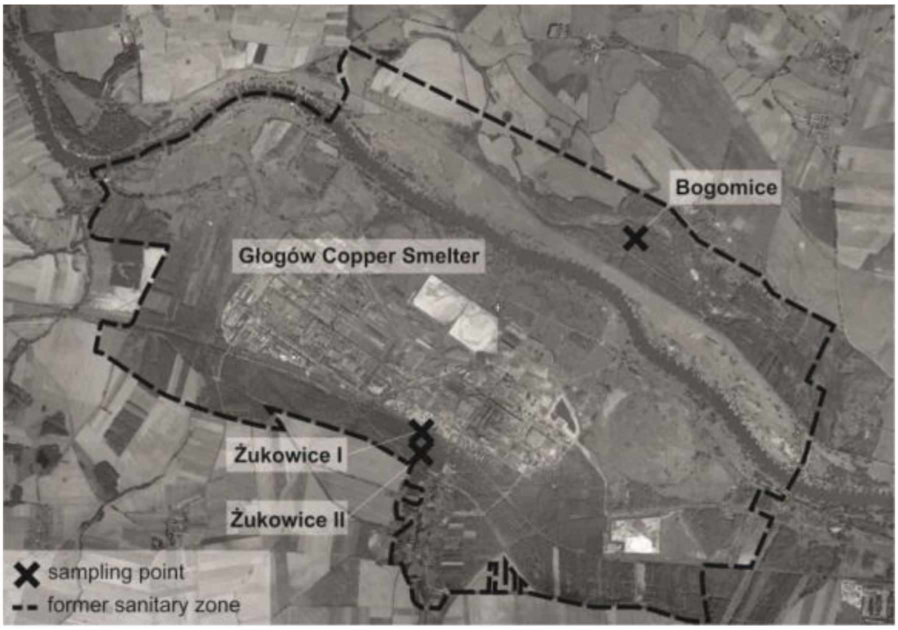

Fig. 1. Location of sampling sites in the protective forest of GCS [20]

GCS is a part of KGHM Polska Miedź S.A. The company works since 1971. The company produce mainly electrolytic Cu – cathodes, crude lead, nickel sulphate and silver, shaft slag, sulphuric acid, granulated slag. The main pollution of this copper smelter are gases (SO_2, CO, NO_x, CS_2, F) and metal dusts containing Cu, Pb, Zn, Cd, As.

Protective zone of the GCS was established in 1987. The purpose of this zone was to compensate the negative impact of the copper smelter on the environment. This include the adjacent areas and the human population living there. The surface of the protective zone was about 2 840 ha. Early works on this site started from 1973. The main species used for this zone was various poplar clones, which nowadays represent approx. 54% of the total forested area.

MATERIAL AND METHODS

Average soil sample were collected for laboratory analysis from all characteristic levels of the soil profile. The soil material was air-dried and sieved through a sieve with a mesh diameter of 2.0 mm. With the material prepared this way, the following analyses were made: particle size distribution – using hydrometer method, pH – in H_2O and 1M KCl suspension (potentiometrically), soil/liquid - 1:2.5, organic carbon – using Tiurin method, Cu, Pb – using atomic absorption spectrometry FAAS after mineralisation in aqua-regia. Averaged samples of unwashed leaves of *Populus robusta* L. were collected in the autumn of 2010. After drying, the leaves were crushed in a mill and mineralized in aqua-regia. The content of Cu, Pb was tested using atomic absorption spectrometry FAAS. Poplar leaves was tested in for 5 consecutive years.

RESULTS

Selected properties of soils samples are shown in table 1. The content of Cu an Pb in poplar leaves is shown in table 2.

Tab. 1. Selected properties of soils samples

Research site	Depth	Sand	Silk	Clay	pH		$Cu_{tot.}$	$Pb_{tot.}$
	cm	%			H2O	1M KCl	$mg\cdot kg^{-1}$	
Żukowice I	0-3	-	-	-	5,9	5,5	5400	1316
	3-26	69	31	0	6,2	6,0	1530	416
	26-47	63	34	3	5,3	4,9	52	304
	47-62	58	33	9	5,5	5,4	45	79
	62-83	83	11	6	5,9	4,4	45	76
	>83	82	18	0	6,4	5,9	38	109
Żukowice II	0-2	85	15	0	6,9	6,6	3450	1015
	2-29	79	21	0	7,8	7,0	958	268
	29-42	78	22	0	7,8	7,1	41	60
	>42	87	13	0	7,9	7,2	100	75
Bogomice	0-3	-	-	-	6,3	5,9	4115	1507
	3-23	65	34	1	5,1	3,8	174	702
	23-40	61	37	2	5,2	3,8	99	114
	40-70	65	34	1	5,7	4,3	85	108
	>70	80	19	1	5,6	4,3	60	106

Tab. 2. The content of Cu and Pb in poplar leaves

Research site	Cu, $mg\cdot kg^{-1}$			Pb, $mg\cdot kg^{-1}$		
	Min	Max	Mean	Min	Max	Mean
Żukowice I	81,7	95,9	73,9	66,6	181	147
Żukowice II	187	189	173	67,5	210	121
Bogomice	121	145	105	108	212	159
SD	43,9	30,8	36,5	47,7	57,7	50,1

CONCLUSIONS

- The main factors influencing the content of heavy metals in the research are the soil reaction and the soil organic matter content.
- The content of Cu and Pb in the topsoil from the former sanitary zone of the GCS exceed Polish threshold values for industrial areas, which is established up to 600 mg kg^{-1} d.m. The soil horizons presented below the topsoil contained significantly lower amounts of heavy metals. A highly significant correlation between Cu, Pb and the soil organic matter content was found.
- The content of Cu and Pb in poplar leaves varies depending on the year, climatic parameters and soil properties. Looking at the trace elements level in tree tissues it is possible to use the phytoremediation technique to clean up the Cu and Pb polluted soil.

PRACTICAL APPLICATIONS OF FERRATES (FE^{VI} AND FE^{V}) IN COMBINATION WITH HYDROGEN PEROXIDE FOR FAST AND EFFECTIVE REMEDIATION OF CONTAMINATED GROUNDWATER

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KEYWORDS
Ferrates, Remediation, Oxidation, Groundwater

ABSTRACT

In recent years, particles of iron in high oxidation states (Fe^{IV-VI}), commonly called ferrates, have been presented as a very effective remediation material especially due to their strong oxidation ability. However, so far the majority of applications have been carried out only as a laboratory tests with model samples in many cases. The real application of ferrates in remediation practice seems to be more complicated than expected and lot of them thus end in failure. Therefore there is a necessity to consider the suitability of their use or consider their possible combination with other agents in order to reach required removal efficiency in remediation practice. This study is focused on practical applications of ferrates during in-situ and ex-situ remediation of groundwater contaminated by a wide range of organic contaminants. The first locality (locality A) was selected for in-situ remediation (Fig. 1(a)). This locality was situated in the area of the factory focused on metal production and main contaminants of the groundwater were chlorinated ethenes (CEs) - total value of CEs (ΣCEs) was ranged 60-70 mg/l. The second locality (locality B) was selected for ex-situ remediation which was carried out as a container test with groundwater pumped out from the borehole (Fig. 1(b)). This locality was situated in the area of chemical factory and the groundwater has been contaminated by a wide range of organic contaminants, of which the most important groups have been aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes) and chlorinated aromatic hydrocarbons (chlorobenzene, o-dichlorobenzene, m-dichlorobenzene, p-dichlorobenzene). All detected organic contaminants including level of their contamination before the start ex-situ remediation are listed in Tab. 1.

Fig. 1(a): in-situ applications on the locality A

Fig. 1(b): ex-situ applications on the locality B

Tab. 2. Contaminants detected in the groundwater of the locality B incl. level of their concentration before start of the test

Contaminant	c (µg/L)	Contaminant	c (µg/L)	Contaminant	c (µg/L)
benzene	340	p-dichlorobenzene	4 900	∑ cresols	50
toluene	363 000	∑ chlorinated ethenes	520	∑ dichlorophenols	9
∑ xylens	480	ethylbenzene	140	∑ chlorophenols	12
1,2,3-trichlorobenzene	62	chlorobenzene	2 900	aniline	730
o-dichlorobenzene	19 000	naphtalene	3 600	N-ethylaniline	4.6
m-dichlorobenzene	3 700	phenol	3.0	2,4,6-trimethylaniline	130

For all applications, a ferrate product ENVIFER from LAC, ltd. (Czech Republic) was used. ENVIFER parameters were as follows: total content of Fe: 18.4 wt%; content of Fe^{V} 57±3 mol%; content of Fe^{VI}< 3 mol%; content of K_2O 19±3 wt%; Fe^{VI}/Fe^{V} ratio after dissolution in water: 0,81 => 1 g ENVIFER ≈ 85 mg Fe^{VI}.

Both applications were carried out as follows: In the first step, ferrate composite ENVIFER was applied and in the second step, approx. one hour later, 35% hydrogen peroxide was applied. In the case of the in-situ remediation (locality A), ferrates were applied directly into selected borehole (Fig. 1(a)) as a concentrated solution prepared by dissolving of 1.75 Kg of ENVIFER in 700 L of tap water. The applied amount of hydrogen peroxide was approx. 15 L. Over the following six months, other three applications of hydrogen peroxide have been realized. In the case of the ex-situ remediation (locality B), ferrates were applied in amount of 350 g of ENVIFER directly into the container with 900 L of the groundwater (Fig 1(b)). The applied amount of hydrogen peroxide was approx. 4.5 L (≈ 5 mL/L). The entire process of ex-situ remediation took 24 hours.

Following figures show substantial results obtained from both applications. Fig. 2 shows the development of the contamination of ΣCEs in the application borehole (locality A) from November 2013 to October 2014 including application of ferrates with hydrogen peroxide (27. 2. 2014) and other three applications of hydrogen peroxide (27. 3., 13. 5. and 12. 8. 2014). Fig. 3 shows total removal efficiency of monitored contaminants at the end of the ex-situ remediation (locality B). Results are compared to a blank sample.

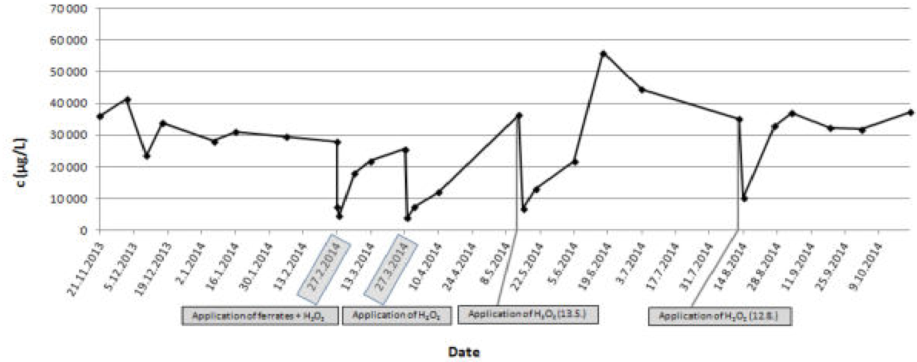

Fig. 2. The development of the contamination in application borehole (locality A) from November 2013 to October 2014 including application of ferrates with hydrogen peroxide (27. 2. 2014) and other applications of hydrogen peroxide (27. 3., 13. 5. and 12. 8. 2014)

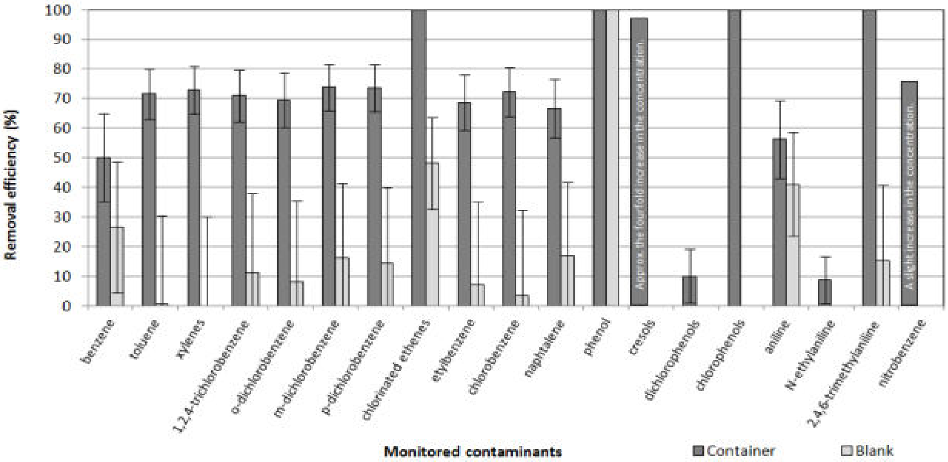

Fig. 3. Total removal efficiency of monitored contaminants at the end of the ex-situ remediation (locality B); compared to a blank

On the basis of obtained results, the combination of ferrates and hydrogen peroxide seems to be very fast and effective with a rapid decrease in the contaminants concentration. During 24 hour reaction time, the majority of detected contaminants was removed from 60-90 %. Moreover, from the viewpoint of the environmental protection, the combination of ferrates with hydrogen peroxide acts as completely green technology, because ferrates are reduced to Fe^{3+}/Fe^{2+} as the form of various polyhydroxy complexes and hydroxides (ferric sludge), which are nontoxic and commonly occurring in the nature, and hydrogen peroxide is degraded to O_2 and H_2O. In addition, the ferric sludge can be used repeatedly. However the use of this combination is more effective for ex-situ remediation than the in-situ remediation. In the case of in-situ remediation the effects are only short-term in consequence of the incessant supply of contamination from the surroundings.

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THE COMPARISON OF BIOLOGICAL DEGRADATION OF POLYCHLORINATED BIPHENYLS AND PHYSICO-CHEMICAL METHODS OF THEIR ELIMINATION

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KEYWORDS

Bacterial strains, biodegradation, polychlorinated biphenyls, zerovalent nanoiron

INTRODUCTION

Polychlorinated biphenyls (PCBs) belong to the most important environmental contaminants. Their physico-chemical properties allow them to persist in the environment and bioaccumulate in lipid-rich tissues of all organisms. Due to their toxicity and classification as a persistent organic pollutant, PCB production has been forbidden in most industrialized countries in the late 1970s. PCBs were produced in Czechoslovakia by chemical plant Chemko in Strážske until 1984. Today east Slovakia belongs to the most PCB contaminated areas in the middle Europe. Effective, but economically disadvantageous way seems to use various physico-chemical methods. A more attractive alternative is an in situ remediation of contaminated soils, waters and sediments through biological processes. The subject of this work is to study the degradation potential of bacterial isolates obtained from contaminated sediment in model mineral media artificially contaminated with PCBs. The work also aim with comparison of the efficiency of the biological process and physico-chemical process of PCB elimination applying zerovalent iron nanoparticles.

MATERIAL AND METODS

Bacterial strains *Achromobacter xylosoxidans* and *Rhodococcus* sp. used in this study were isolated from long-term contaminated area in surroundings of the former producer of PCBs Chemko Strážske (Dudásová et. al, 2014). PCB degradation was determined using the commercial mixture DELOR 103 (Chemko Strážske, Slovakia).

Bacterial inocula were prepared by growing used strains according to Dudásová et al. (2014) on a rotary shaker 180 rpm for 48 h at 28 °C. The medium contained 60 mg of biphenyl to stimulate PCB degradation ability. 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 Dudásová et al. (2014). DELOR 103 was added to each flask as solution in DMSO at a final concentration of 100 mg.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 (Dercová et al., 1998). Flasks were incubated at 28 °C on a rotary shaker for required amount of days (1, 3, 5, 6).

Experiments of elimination of PCBs by addition of nanoparticles of zerovalent iron were performed in steril apparatus in 100 ml of MM medium with addition of DELOR 103 (100 mg.l^{-1})and nanoiron oil suspension Nanofer (2 g.l^{-1}; Nanoiron, CZ).

PCBs were extracted from the liquid phase of the medium twice with n-hexane for the both sets of experiments.

PCBs were analyzed by gas chromatography GC (Agilent 7890A) 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), a 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 according to Mills (2007).

RESULTS AND DUSCUSSION

Biodegradation of PCBs by bacterial strains

The aim of this part of the work was monitoring of PCB degradation process in time - kinetics of biodegradation - using two bacterial strains *Achromobacter xylosoxidans* and *Rhodococcus* sp. Based on the obtained results it can be concluded that with prolonged cultivation time the biodegradation for most of the PCB congeners was increased. Biodegradation of total analyzed PCB congeners was 61% by strain *Rhodococcus* sp. and 57% by *Achromobacter xylosoxidans* (Fig. 1). A positive finding was that the most marked decline of PCB congeners compared to the initial concentration occurred immediately after the first day of cultivation by both strains for all analyzed PCB congeners.

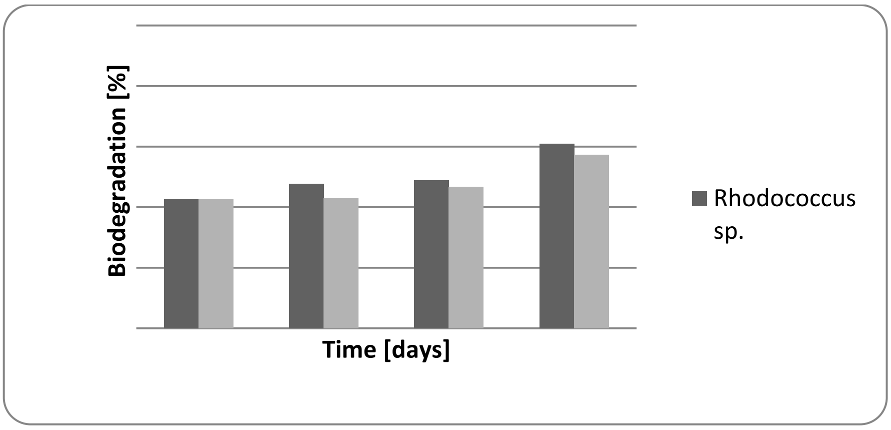

Fig. 1. Biodegradation of total analyzed PCB congeners in time by bacterial strains *Rhodococcus* sp. and *A. xylosoxidans*.

Elimination of PCB using nanoparticles of zerovalent iron (ZVI)

The reductive dehalogenation effect of nanoparticles of ZVI on elimination of PCBs after three and six days of cultivation was observed. As it can be seen in Fig. 2, a significant difference in elimination values was achieved. More adventageous and more efficient procedure of PCB elimination appears to be, regarding to the lenght of the experiment, cultivation for six days with oil suspension of Nanofer. The elimination of total analyzed PCB congeners was amounted up to 77%.

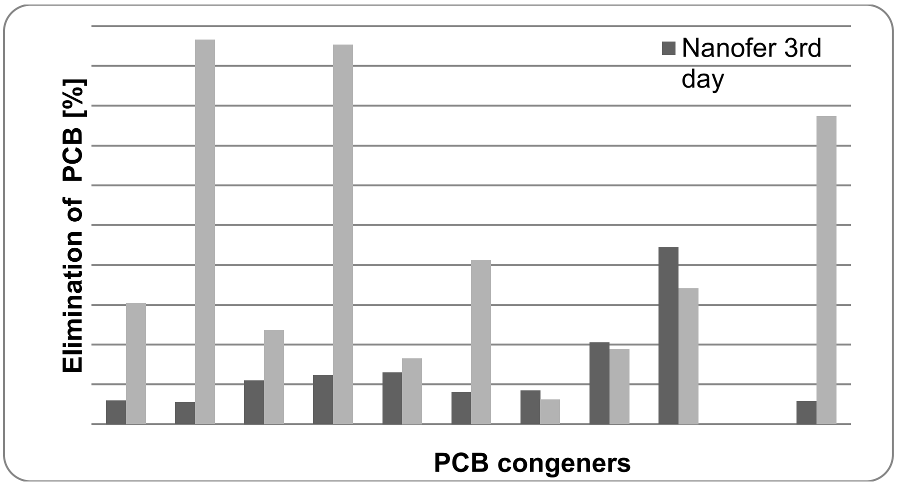

Fig. 2. Elimination of PCB congeners in time by using nanoparticles of zerovalent iron Nanofer.

CONCLUSIONS

The biological method of bacterial strain addition, bioaugmentation, is considered as one of the possible approaches for increasing biodegradation ability of natural microorganisms in contaminated area. It was confirmed that used bacterial strains *Achromobacter xylosoxidans* and *Rhodococcus* sp. are suitable degraders with about 60% degradation value of PCBs. The addition of zerovalent iron nanoparticles Nanofer had higher efficiency of PCB elimination (77%). Both approaches can be applied depending on the contaminated matrix and hydrogeological conditions.

ACKNOWLEDGEMENT

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ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS CONTAMINATION IN URBAN TOPSOILS OF BRATISLAVA

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KEYWORDS

Urban soil, potentially toxic elements, contamination, Bratislava, index of geoaccumulation

ABSTRACT

The contamination of urban soils by potentially toxic elements (PTEs) is one of the fastest growing types of environmental contamination due to vehicle emissions, industrial discharges and other activities. The main goal in this study was to calculate the soil contamination by potentially toxic elements (PTEs) (namely Cu, Zn, Pb, As, Cd, Hg) in urban soils in Bratislava via index of geoaccumulation (I_{geo}). Based on the average value of geoacummulation index (I_{geo}) of each PTEs, we found that the soil samples belonged to categories of uncontaminated ($I_{geo} \leq 0$) and uncontaminated to slightly contaminated (I_{geo} 0 – 1) soil but there were several contaminated sites concentrated mainly in the District I and Distict III belonging to categories of slightly contaminated(I_{geo} 1 – 2) and moderately to strongly contaminated(I_{geo} 2 – 3) soil.

INTRODUCTION

Soil contamination of urban areas by potentially toxic elements (PTEs) becomes one of the most environmental concerns worldwide. The soil concentration of these elements depends on the composition of parent rock and on the anthropogenic inputs. For the assessment of soil contamination, geoaccumulation index (I_{geo}) was used in this article.

MATERIALS AND METHODS

A total of 95 surface soil samples (0-10 cm) were taken from different land use areas in Bratislava city (Districts I. – V.) (Fig. 1) and analyzed for basic soil properties and concentrations of selected PTEs in an accredited laboratory (Cu, Cd, Pb, Zn by inductively coupled plasma-atomic emission spectrometry ICP-AES; Hg by atomic absorption spectrometry AAS-AMA and As by atomic absorption spectrometry AAS with hydride generation).

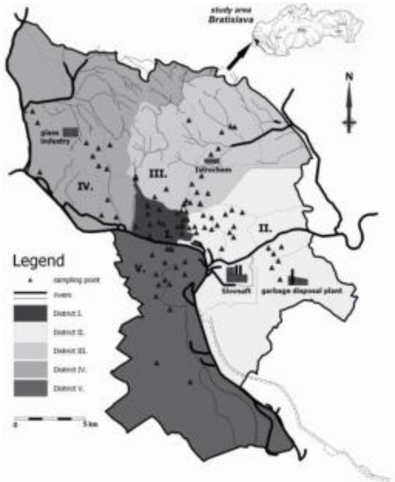

Fig. 1. Locations of sampling sites in Bratislava

For the assessment of soil contamination, geoaccumulation index was used and calculated as follows [I.]:

I. $$I_{geo} = \log_2 \frac{C_n}{1{,}5 \times B_n}$$

where $C_n$is the concentration of monitored PTE in soil, B_n is the background concentration of PTE in soil and 1,5 is constant. Muller (1969) has characterized the following six classes of I_{geo}: $I_{geo} \leq 0$ uncontaminated, I_{geo} 0-1 uncontaminated to moderately contaminated, I_{geo} 1-2 moderately contaminated, I_{geo} 2-3 moderately to strongly contaminated, I_{geo} 3-4 strongly contaminated, I_{geo} 4-5 strongly to extremely contaminated, $I_{geo}> 5$ extremelly contaminated.

RESULTS

The calculated results of geoaccumulation index are displayed in Tab. 1. According to the average value of geoacummulation index (I_{geo}) of each PTE, the soil samples belong to categories of uncontaminated ($I_{geo} \leq 0$) and uncontaminated to slightly contaminated (I_{geo} 0 – 1) soil but there were several contaminated sites concentrated mainly in the District I and Distict III, which belonged to categories of slightly contaminated(I_{geo} 1 – 2) and moderately to strongly contaminated(I_{geo} 2 – 3) soil. The higher maximal value of I_{geo} was found in District I. – the old city centre a District III. – the industrial city area. In District I., three slightly contaminated(I_{geo} 1 – 2) soils for Zn, Pb and Hg and two moderately to strongly contaminated(I_{geo} 2 – 3) soils for Zn, Pb and Cd were identified. Nine slightly contaminated(I_{geo} 1 – 2) soils for Cu, Zn, Pb and Cd, and three moderately to strongly contaminated(I_{geo} 2 – 3) soils for Cu were found in District III.

Tab. 1. Minimal, maximal and average value of geoaccumulation index for each potentially toxic elements in each District

	District I. Soil samples - 15			**District II.** Soil samples - 22			**District III.** Soil samples - 28			**District IV.** Soil samples - 14			**District V.** Soil samples - 16		
I_{geo}	Min	Max	Av	Min	Max	Av	Min	Max	Av	Min	Max	Av	Min	Max	Av
Cu	-1.08	1.03	-0.09	-1.71	0.25	-0.61	-1.49	2.63	0.21	-2.00	1.21	-0.91	-0.87	-0.03	-0.32
Zn	-0.52	2.74	0.44	-1.03	1.35	-0.24	-1.52	1.41	-0.20	-1.83	1.37	-0.87	-0.84	0.31	-0.28
Pb	-1.20	2.23	-0.01	-1.04	0.60	-0.32	-1.64	1.58	-0.48	-1.58	0.71	-0.40	-0.93	0.61	-0.33
Cd	-0.58	2.49	0.61	-2.00	1.45	0.06	-2.00	1.22	-0.06	-1.00	0.62	-0.31	-1.38	1.26	0.50
As	-1.29	0.27	-0.58	-2.09	0.20	-0.87	-1.38	0.52	-0.45	-1.88	-0.06	-0.84	-1.07	-0.07	-0.44
Hg	-1.08	1.67	-0.01	-2.53	1.51	-0.98	-2.73	0.84	-0.56	-1.64	1.03	-0.53	-0.64	2.32	0.42

The highest I_{geo} values were calculated for District I., where the highest total concentrations of PTEs in soils were also measured. This result indicated the historical and land use area trend becasue the city centre (District I.) and industrial areas (District II. and III.) had higher total concentration of PTEs contrary to remote suburban areas (District IV. and V.) mainly used as residential zones.

District III. is also characteristic with higher total concentration of PTEs in soil. Moderate to strong contamination of soil by Cu in this district can be explained by the vicinity of vineyards, in which copper sulphate is used as fungicide, and by the vicinity of traction line where Cu is a component of materials used in manufacture of tramlines and electrical wire.

Moderately contamination of soils for Pb, Cd and Zn in each District can be explained by traffic emmisions.

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CHZJD LANDFILL IN VRAKUNA – THE SLEEPING LOAD OF BRATISLAVA

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KEYWORDS
Environmental load, contaminant, waste, groundwater,

ABSTRACT

The landfill in Vrakuna – The landfill of chemical waste of Juraj Dimitrov Company (CHZJD) is one of the old environmental loads in the capital of Slovakia - Bratislava, which has not yet been given sufficient attention in relation to its possible significant impact on the surrounding environment. The landfill has a crescent shape and its surface is about 46 500 m^2. It is estimated that the volume of waste is about 90 000 m^3. Approximately 65% of the area of the landfill is owned by the Bratislava city and the rest of the territory was sold off to private owners. The fact that 35% of landfill is owned by private persons and companies will lead to potential problems in the process of potential future redevelopment.

Fig. 1. Location of landfill (red point on the left) in the Bratislava region and the detail location (red area on the right) in the part of Bratislava city named Vrakuňa

The landfill was established in the old river bed of Malý Dunaj by decision of the local authority in Bratislava no. 1059 / 405-66 dated 14.7.1966. Storage of waste began in 1966. Waste was traceable in layers until the 1979. In 1980, the entire landfill was covered with an inert material with thickness of about 2-6 meters. Before running the Gabčíkovo power plant there was no interference between waste and ground water level in the area of landfill. The groundwater level in the whole area from Gabčíkovo to Bratislava in 1996 rises after starting of Gabčíkovo power plant. There is regularly to the process of leaching of waste to groundwater since 1996. So it means 30 years of active moving of contaminants to the soil, ground water and to the environment.

Because of the potential risk to the environment and the people living in this area has been the burden placed at the list of priority loads specified for a detailed investigation of the environment, which is part of the Ministry's geological work titled "Investigation of contaminated sites in selected locations of the Slovak Republic" parts "An investigation of the environmental burden in Bratislava Region: Vrakunská cesta - landfill CHZJD ".
At the site is still phase of the survey actual. In connection with occurrence of drilling techniques at a landfill and collection of water samples from nearby boreholes and wells by samplers from geological company there occurs an increase of activity and interest of local citizens. Over 30 – years it became a place for hauling garbage, instead of living for several people without home and seemingly "green" nature corner stretching between the

two city blocks. After 30 years of silence there are realising an active exploratory works which can help to the good solving of this area.
The site has already taken place with geophysical measurements to map out the course and limit the landfill, and the place adjacent depressions, which in the past served to store various kinds of waste. At the landfill was built 9 monitoring wells ranging up to Neogene clayey subsoil. Of the wells were collected groundwater sample for evidence of the alleged wide range of pollutants of environmentally hazardous. In total, about 500 samples were analysed for heavy metals, volatile compounds, oils, pesticides and herbicides, and many other substances that could explain the current conditions of the potential environmental risk (Chovanec, 2014).

In the past took place at the site several engineering-geological, hydrogeological and geological surveys environment. The aim of this work was not conceptual mapping of landfill and the environment, but in the most cases this was only a partial implementation of surveys for other purposes. The pollution recognized in the past was manifested by increasing of concentrations mainly sulphates, chlorides, total petroleum hydrocarbons, and from organic spectrum were the highest - cyclohexane derivatives and benzothiazole (Pospiechová 1991, Klaučo 1982, 1983, 2000, Vlasko et al. 2000, etc.).

In connection with the hypothesis of a possible penetration of pollutants through the city part Vrakuňa, above the Malý Dunaj to the big Slovak groundwater reservoir with name „Žitný ostrov“ was performed sampling boreholes and wells in Vrakuňa and surrounding area in direct of groundwater flowing. Currently are realising laboratory analytical works. During the field works and mapping of the site and the surrounding area has been found that some residents and gardeners are still using the water from their own wells for irrigation and the growing of fruit and vegetables. The using of groundwater for drinking and irrigation in this area was prohibited before several years.

The results from actual investigation works will brings a lot of answers to actual question about this landfill and also a new materials and documents for local government which can realise next steps to process of redevelopment.

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IMPACT OF CALCIUM AND MAGNESIUM ON HEALTH STATUS (SLOVAK REPUBLIC)

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KEYWORDS
Health status, groundwater, soil, calcium, magnesium, Slovak Republic

ABSTRACT

The presented study deals with the analysis of relationship between list of contents of Ca, Mg in soils/ groundwater and the data on relative mortality for cardiovascular diseases (REI), indirect standardized mortality ratio (SMRI) and potential years of life lost for cardiovascular diseases (PYLLI) in Slovak Republic. The statistical method for identification of relationship was calculated with the mean values (health and chemical data) for each of 2883 residences. Statistical methods as a linear regression and Spearman correlation were used for model of relation data analysis. Based on the results of calculations counted by both of mathematic methods contents of calcium, magnesium were defined as a significant parameter for REI, SMRI and PYLLI. The correlation coefficients are suggestive of necessary chemical parameters for better health status in case of mortality to cardiovascular diseases. At these results the relative mortality reaches the highest correlation relationships with concentration of magnesium and calcium in groundwater and soil in the Slovak Republic. These coefficient values are the most significant among of all: for chemical parameter Mg in groundwater toward REI -0,174 and REI -0,113 in soil; for contents of calcium in groundwater toward REI -0,144.

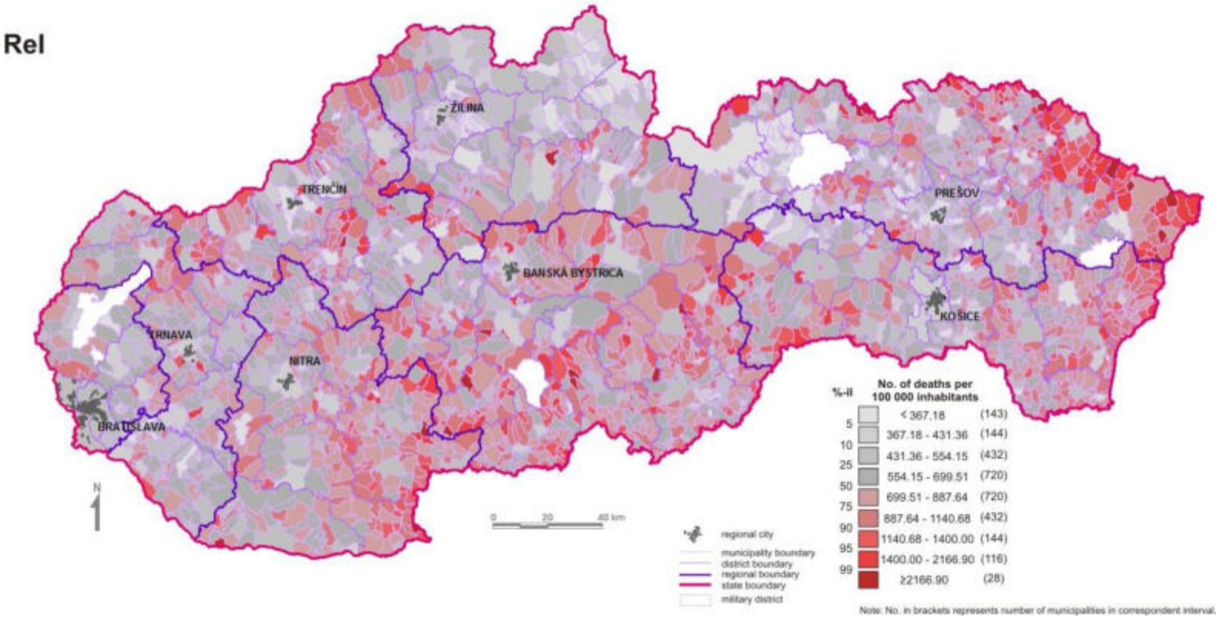

Fig. 1. Health indicator – REI (deaths per 100 000 inhabitants/cardiovascular diseases) for municipalities in Slovak Republic

The association of human health and calcium and magnesium as a macroelements in natural background has been known since antiquity. The relationship between the concentration of calcium and magnesium in the groundwater and soil to human health is wide-spectrum recognized and assessed in a lot of scientific studies and books (Yang et al., 2006; Rosanhoff, 2013;Mahaney et al., 2000).

In this study we use a geochemical database from geochemical mapping of Slovak Republic (soil/groundwater analysis) and health indicator data (mortality to cardiovascular diseases, Fig. 1) were received from the databaseof the Statistical Office of the Slovak Republic (Rapant et al., 1996). Health indicators include REI (deaths per 100 000 inhabitants/cardiovascular diseases), SMRI (indirect standardization (to age): standardized mortality ratio to cardiovascular diseases) and PYLLI (potential years of life lost due to cardiovascular diseases per 100 000 of population).

Relation data analysis was processing during linear and Spearman correlation. The results of calculating correlation coefficients are shown in Tab. 1. Assessment of relationship between health indicators and content of calcium and magnesium in soil and groundwater was presented with strong significance and impact of Ca and Mg was observed.

Tab. 1. Linear (r) and Spearman (R) correlation coeffcients for calcium and magnesium in groundwater and soil (*)

rank	**parameter**	**r**	**α**	**significance**	**R**	**α**	**significance**
1.	**Ca&REI**	**-0,149**	0,000	+++	**-0,144**	0,000	+++
2.	**Ca&SMRI**	**-0,045**	0,066	-	**-0,039**	0,114	-
3.	**Ca&PYLLI**	**-0,069**	0,005	++	**-0,116**	0,000	+++
4.	**Mg&REI**	**-0,157**	0,000	+++	**-0,174**	0,000	+++
5	**Mg&SMRI**	**-0,037**	0,128	-	**-0,057**	0,020	+
6.	**Mg&PYLLI**	**0,045**	0,060	-	**-0,121**	0,000	+++
7.	**Ca&REI***	**-0,053**	0,018	+	**-0,059**	0,015	+
8.	**Ca&SMRI***	**-0,033**	0,009	+	**-0,049**	0,046	+
9.	**Ca&PYLLI***	**-0,016**	0,011	+	**0,037**	0,134	-
10	**Mg&REI***	**-0,054**	0,007	+	**-0,113**	0,000	+++
11.	**Mg&SMRI***	**-0,072**	0,005	++	**-0,091**	0,000	+++
12.	**Mg&PYLLI***	**-0,024**	0,008	+	**0,021**	0,387	-

The concentration of calcium and magnesium in groundwater have shown as a more significant parameter for better health status than in soils, where we can notice lower correlation coefficients. These coefficient values are the most significant among of all: for chemical parameter Mg in groundwater toward REI -0,174 and REI -0,113 in soil; for contents of calcium in groundwater toward REI -0,144.

Approximately 90% inhabitants of Slovak Republic were used a groundwater for drinking usage and this fact can lead to observation of intake Ca and Mg to human body and their impact on human health status especially for mortality to cardiovascular diseases. The voluntary intake of essential macroelement to human body during soil ingestion is not observed for Slovak inhabitants (geophagy).

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TWO PROGRESSIVE PROCEDURES FOR CONTAMINANT REMOVING FROM THE SUBSURFACE AND A NON-INVASIVE METHOD OF CONSTRUCTION SUBSURFACE CLEANING

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KEYWORDS
Environmental nanotechnology, iron particles, microbial reduction, induction heating, microwave chemistry, volatile contaminants

ABSTRACT

CHEMCOMEX Praha, a.s. is a large company particularly focused on nuclear power industry and engineering. One division of CHEMCOMEX - Division of Geology and Remediation - has been involved in geological issues since the company was established. CHEMCOMEX is market leaders in all kinds of geological survey in the Czech Republic. Division of Geology and Remediation offers hydrogeological survey, geotechnical survey, risk assessment and remediation technologies of the contaminated areas. R&D activities of CHEMCOMEX (cofinanced in some cases by public funds, for instance TAČR) allows to enhance the business portfolio in the sector of environmental products and services.

In this paper, a technology IRON, which is based on a synergic link between abiotic contaminant reduction using in situ applied suspension of Fe(0)particles and subsequently applied mixture bioaugmentation agent for degradation process promotion (based on biological reduction of iron). The technology is designed to overcome the situation of DCE-stall and it eliminates typical residues of chlorinated ethylene on contaminated sites. The second example, VLNOCHOD device, deliberately conceived as a diametrically different example, presents the concept of mobile technical equipment for local desorption of a surface contamination on building and construction surfaces using induction heating (microwave thermal desorption). Using this solution, the vast majority of hazardous substances (capable to be volatilized at higher temperatures) can be successfully removed with safe measures.

Fig. 1. Mobile system of IRON *Technology* (left) and its anaerobic reactor (right)

In situ reductive technology had their massive boom in recent years. Despite some very satisfactory results, their key deficiencies are fully reflected, which include the high price of iron nanoparticles, as well as a rapid decline in their reduction ability due to storage, handling, logistics and applications as well as restrictions on migration properties of nanoparticles in the groundwater system. IRON technology was based on the own experience with in situ reduction technology and a thorough analysis of the strengths and weaknesses of reducing nanotechnology and especially thorough assessment of the threats and opportunities that are associated with them. A specific example is the opportunities differently sized bodies of the oxidized iron in the form of clusters and clusters that remain in the immediate vicinity of hydrogeological objects. In nature, it occurs a group of microorganisms, which carry out anaerobic respiration associated with using ferric compounds, i.e. iron-reducing bacteria (Ehrlich 2009). Their metabolism does not require any specific delivery of various substances. Metabolic sources are merely simple compounds to cover carbon, energy, and reducing equivalent requirements such as acetate, hydrogen, chlorinated ethylenes with fewer chlorine atoms or alcohols and lower fatty acids, which arise spontaneously while organic matter has been decomposed. The technology IRON is an example of treatment train process, which consists of abiotic delivery (supply of a reducing agent) and bioaugmenation application of suspension comprising three iron-reducing bacteria taxa. Laboratory and especially pilot tests in field applications have shown that the IRON technology is a very effective tool in similar situations like a DCE stall effect. Its undeniable advantages include cost reductions in the operational phase of the less need for expensive application agents replacing them with biological suspensions. The technology requires experience with anaerobic remediation technologies.

Fig. 2.VLNOCHOD *Microwave remediation device*

VLNOCHOD system is innovative remediation technology as the solution for contaminated surfaces. The decontamination is based on direct microwave heating of small surface under the open applicator, the evaporation of semivolatile organic contaminants, vacuuming of contaminant vapors and the consequent treatment of contaminated air. All technological parts are placed in one compact device on the roar which is simply transportable over and between the contaminated sites. The movement of the rover over the site and the sequential decontamination of surface provide the remediation of larger area. Currently, both technologies have been tested, optimized and verified to become effective, fast, environmental friendly and safe instrument. Both technologies are patented.

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TOXIC EFFECTS OF TRACE ELEMENTS ON MALE REPRODUCTIVE HEALTH

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KEYWORDS
Trace elements, male reproductive health, reactive oxygen species, lead

ABSTRACT

Fertility in humans is a complex property that depends on the female and male reproductive capabilities, which are result from the interaction of physiological, genetic, behavioral factors and environmental influences. According to WHO, 8-12% of couples are infertile. The prevalence of infertile marriages in European countries is around 10%, in the USA - about 15%, in Russia - 17.5%. For a long time trace elements are divided into essential and toxic. However, "essential" microelements at high concentrations can cause toxic effects, and "toxic" under certain concentrations may be necessary for normal physiological processes, which is in accordance with the law of ecological optimum. In our work, we will focus only on the toxic effect of trace elements associated with their high concentrations in the body. Our presentation covers the data on the toxic effects of trace elements on the male reproductive system. The basic pathogenic mechanisms of male infertility are described. Different points of view on the effect of high concentrations of trace elements on components of endocrine system functions, male reproductive tract, properties of gametes and state of their genetic material are showed.

INTRODUCTION

Male reproductive health has deteriorated considerably in the last few decades. In recent years, there has been growing concern regarding the adverse effects of various environmental contaminants on male reproduction. Most environmental toxicants have been shown to induce reactive oxygen species (ROS), thereby causing a state of oxidative stress in various compartments of the testes (Wong EW, Cheng CY., 2011). In sperm, ROS are produced by both spermatozoa and circulating leucocytes and may be part of normal adaptive reactions, such as the capacitation process. However, a number of external toxicants may also contribute to ROS production in the testis and epididymis, leading to a decrease in sperm viability and motility and, therefore, an increased onset of the male factor of infertility (Lavranos G., et al., 2012). The present study summarizes recent papers on environmental contaminants and male health.

POSSIBLE MECHANISMS OF ENVIRONMENTAL TOXICANTS ACTION

The most discussed issues regarding male infertility are:
1) State of endocrine “hypothalamus-hypophysis-testis” axis; 2) State if male reproductive tract; 3) Sperm counts and sperm quality; 4) Genetic mutations.
Environmental toxicants, especially heavy metals and organic chemicals of synthetic and microbiological origins, disrupt hormone production and action in the mammalian testes. Endocrine disruption leads to disorders of testicular function and thereby compromises the normal phenotypic development of male sexual characteristics, initiation and maintenance of spermatogenesis. The toxicants also induce impairment of testicular cells function, testicular histology, and sperm cells function directly (Manfo FP, Nantia EA, Mathur PP., 2014). Environmental contaminants can mimic natural estrogens and target testicular spermatogenesis, steroidogenesis, and the function of both Sertoli and Leydig cells (Mathur PP, D'Cruz SC., 2011).
Although acute exposure of toxicants contributes to apoptosis and necrosis of testicular cells, chronic and sub-lethal exposure is prevailing in the general public (Hauser R, Sokol R., 2008). Increase in oxidative stress can be seen in up to 80% of clinically proven infertile men, and exposure to environmental toxicants is a major factor contributing to such increase (Tremellen K., 2010). Environmental toxicants that have been shown to induce oxidative stress in the testis are highly heterogeneous, with different chemical structures, and include cadmium (Liu J, et al, 2009), bisphenol A and 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (Jin MH, et al., 2008).

IMPACT OF DIFFERENT POLLUTANTS ON MALE HEALTH

Epidemiological studies suggest awareness of environmental factors which may affect semen quality (Jurewicz J, et al, 2009) and recently published paper confirm this opinion. Thus, computer aided sperm morphometric assessment was undertaken on morphology slides obtained as part of a multi-centre study in 1999-2002 of occupational factors in male infertility. Men attending 14 fertility clinics across the UK were recruited and gave a semen sample. Before results of the semen analysis were known, the men completed detailed questionnaires about their employment and lifestyle. Occupational exposures were assessed by occupational hygienists. Morphology results were available for 1861/2011 men employed at the time of recruitment. Poor morphology, adjusted for confounding, was related to self-reported lifetime exposure to lead (OR=1.33; 95% CI 1.00 to 1.75). Low motile sperm count was also related to self-reported lead and to hygienist-assessed glycol ether exposure. Self-reported use of paint stripper (OR=1.47; 95% CI 1.07 to 2.03) and lead, but not glycol ether, were significantly related to the combined case definition (Cherry N, et al., 2014).

Lead causes male reproductive impairment among painters. A case series of 27 infertile painters were subjected to semen analysis, measuring of blood lead level (PbB) and serum levels of endocrinal parameters including follicle-stimulating hormone (FSH), luteinising hormone (LH), testosterone (T) and prolactin (PRL). Significantly lower sperm count and motility were found in those with duration of exposure (≥ 15 years), but no significant difference was found for PbB and serum levels of FSH, LH, PRL and T (Hosni H, et al., 2013).

Chronic environmental exposure to low levels of lead adversely affects the spermatic quality (Morán-Martínez J, et al., 2013). In the study conducted in Taiwan was found that higher semen lead concentration was correlated with lower sperm count, but not with semen volume, sperm motility or sperm morphology as assessed by simple linear regression. Interestingly, that all 341 subjects were married and from infertile couples without occupational exposure to lead (Wu HM, et al., 2012). Moreover, it was shown that lead toxicity induces cell stress in cardiofibroblasts, and protective autophagy is activated by inhibtion of mTORC1 pathway (Sui L, et al., 2015).

Occurrence of two heavy metals, arsenic and cadmium (Cd), have been reported in the drinking water and seminal plasma of infertile male patients as compared to a control group in Southern Assam, India. The study reports an inverse relationship between total sperm count and heavy metal content in drinking water as well as seminal plasma of the subjects (Sengupta M, et al., 2013). Nectin-2 a junction molecule found at the basal and apical ectoplasmic specializations for the formation of the blood-testis barrier was the direct molecular target of Cd (Zhang X, Lui WY., 2014).

All studied metal ions (mercury (Hg^{+2}), lead (Pb^{+2}), silver (Ag^{+2}), tin (Sn^{+2}), bismuth (Bi^{+3}) and indium (In^{+3}), at levels of 60 mg ml-1 may reduce normal human sperm metabolism by inhibition of sperm creatine kinase, which probably is an important cause of infertility in men (Ghaffari MA, Motlagh B., 2011). The evidence for the adverse effects on reproductive male health of low exposure was strongest for cadmium, lead, and mercury and less certain for arsenic (Wirth JJ, Mijal RS., 2010).

Bacterial reverse mutation tests and chromosomal aberration tests in cultured mammalian cells performed according to standard procedures showed genotoxicity of antimony in both tests, and bismuth also showed positive results in the chromosomal aberration test. In contrast, lead, indium, and silver were considered to be inactive by the criteria of the study completed in Japan (Asakura K, et al., 2009).

“HELPFUL” TRACE ELEMENTS AND WHAT CAN WE DO

Zinc has antioxidative properties and plays an important role in scavenging reactive oxygen species. Element concentrations in seminal plasma of all groups (fertile, infertile, smokers or nonsmokers) were in the order Na > K > Ca > Zn > Mg. Fertile subjects, smoker or not, demonstrated significantly higher seminal Zn levels than any infertile group. A trend was observed for a lower Zn levels in seminal plasma of smokers compared with nonsmokers. Seminal Zn in fertile and infertile (smokers or nonsmokers) males correlated significantly with sperm count and normal morphology of sperm. There was a significantly positive correlation between seminal Zn with Ca ($P < 0.01$) and K ($P < 0.01$) levels in all specimens (Colagar AH, et al., 2009).

It was shown that male partners of infertile couples had reduced level of antioxidative activity, selenium and zinc in their seminal plasma. Most importantly, reduced selenium levels were evident in all patient groups regardless of inflammation status. Therefore, these patients might gain some benefit from selenium supplementation (Türk S, et al., 2014). Recently published review highlights the evidence for protective effects of essential metals, vitamins, edible plants, phytochemicals, probiotics and other dietary supplements against Cd and Pb toxicity (Zhai Q, Narbad A, Chen W., 2015).

CONCLUSION

Several studies have clearly demonstrated that environmental contaminants cause an imbalance in the pro-oxidant and antioxidant status of the testis. Normal testicular spermatogenesis and steroidogenesis are sources of ROS. Although physiological levels of ROS are needed for spermatogenesis, an excess of ROS resulting from environmental contaminants can have deleterious effects. In addition, oxidative stress has also been associated with pathological levels of apoptosis in germ cells and Leydig cells. Future research should be directed towards studying the apoptotic effects of all toxicants that are commonly present in the environment.

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HEAVY METAL CONTAMINATION IN WATER AT LIBIOLA ABANDONED COPPER MINE

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KEYWORDS
Contamination, dump-field, heavy metals, water.

ABSTRACT

By studying past literature and by inspecting Libiola mining area, we elaborated an investigation plan in order to characterize the environmental matrices there. The knowledge of the pollution situation can give us useful indications about the influence of mining activities on the surrounding environment. Starting from considering valley of Gromolo Stream as the largest area to be investigated, we inspected the zones included in the mentioned valley which, according to our preliminary study, could be mostly affected by mining activity, and we also collected some water samples in order to check contamination by heavy metals. Libiola mining site was chosen for our study among other Italian abandoned copper mines because of its geological, environmental and mining features; of its representativeness among other mines; because of available data and contamination aspects.

ARTICLE

Among the Cu ores located in Italy, Libiola has surely a special historic importance. Mineralization there is mainly associated to pillow basalts and basaltic breccias and, subordinately, to serpentinitic rocks from ophiolites of Internal Ligurian Units belonging to the "Supergruppo della Val di Vara" Unit. The primary mineralogic association is there pyrite and chalcopyrite, with subordinate sphalerite, pyrrhotite, marcasite, hematite, mackinawite, magnetite, cubanite, and gold. Scarce gangue minerals include quartz and carbonates.
After identifying the possible polluting sources, the second step was the identification of the potential migration pathways of contaminants from sources to targets and, accordingly, the selection of representative sampling points.

The sampling points from which we collected our water samples are indicated in Fig. 1.

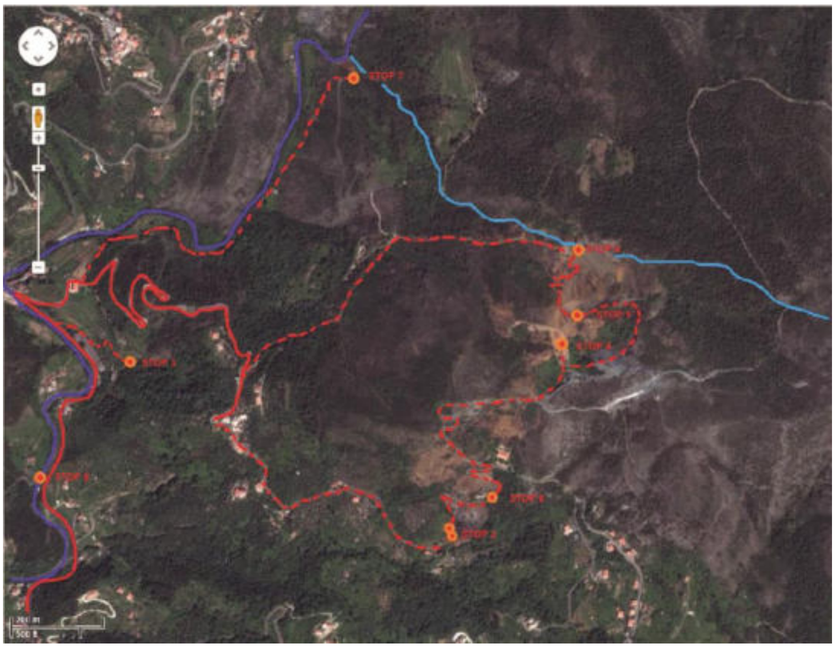

Fig. 1. Location of sampling points at Libiola mining area. Map realized by Google. W1 was collected from the mouth of *Castagna* Gallery (72 m a.s.l., STOP 1, coordinates 44.303215, 9.436215).W2 was collected from basic water flowing out of *Margherita* Gallery (206 m a.s.l., STOP 2, coordinates 44.300015, 9.44505). W3 was collected from the mouth of *Santa Barbara* Gallery, 243 m a.s.l. (STOP 3, coordinates 44.300633, 9.446107).W4 was collected some meters downstream of *Speranza* Gallery's mouth, 291 m a.s.l. (STOP 4, coordinates 44.304188, 9.448467).W5 was collected from the creek river draining the discharge, 238 m a.s.l. (STOP 6, coordinates 44.305424, 9.448500). W6 was collected from *Ida* Gallery, (STOP 7, 106 m a.s.l., coordinates 44.308768, 9.442325).

Concentrations of 14 elements (As, Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, Sn and Tl) were determined in sample by using a simultaneous ICP–OES (Varian ICP/VISTA MPX) equipped with a cyclonic spray chambers. Table 1 reports results from Libiola mining area from ICP-OES analysis in comparison with limit values for groundwater provided by the Italian Law 152/06. In spite of the mere scientific end of our study, nevertheless we found useful to report National law limits for a comparison. Table 2 shows temperature and pH values measured on field at *Libiola* mining area.

Tab. 1. Concentration values concerning water samples collected at Libiola mining site, compared with Italian law limits provided by the Italian Law 152/06 for groundwater.

Element	Unit	W1	W2	W3	W4	W5	W6	Law Limits
As	µg/L	< 15	< 15	< 15	< 15	< 15	< 15	10
Bi	µg/L	2.4	8.1	14	12	<0.1	3.5	-
Cd	µg/L	55	20	15	9.2	1.0	50	5
Co	mg/L	1.1	0.21	0.32	0.16	0.01	0.91	0.05
Cr	µg/L	708	< 5	< 5	14	10	354	50
Cu	mg/L	93	8.0	9.4	11	0.51	54	1.0
Fe	mg/L	366	0.04	0.06	8.4	0.07	284	0.20
Mn	mg/L	4.6.	1.3	1.7	1.1	0.05	3.9	0.05
Ni	mg/L	3.2	0.77	0.46	0.31	0.096	1.8	0.02
Pb	µg/L	< 10	< 10	< 10	< 10	< 10	< 10	10
Sb	µg/L	< 10	< 10	< 10	< 10	< 10	< 10	5
Se	µg/L	< 20	< 20	< 20	< 20	< 20	< 20	10
Sn	µg/L	1.9	1.5	1.5	3.3	2.3	5.1	-
Tl	µg/L	-	-	-	3.7	1.0	-	2

Tab. 2. Temperature and pH values measured on field at Libiola mining area.

Values	W1	W2	W3	W4	W5	W6
T °C	12.6	14.9	14.4	14.8	12.3	13
pH	3.06	5.52	4.94	5.25	6.24	3.06

CONCLUSIONS

The presence of heavy metals at abandoned copper mines is given by ore composition assemblage and it can become a very important source of contamination for the surrounding environment. Water analysis showed different rates of pollution according to the location of collected waters. Main contamination with heavy metals in analyzed water is represented by presence of Cd, Co, Cr, Cu, Fe, Mn and Ni because of presence of tailings containing high levels of ore minerals. In the case of Ni, all collected samples exceed law limits. Water collected from two of the several galleries of the complex, *Castagna* and *Ida*, shows the lowest pH and the highest pollution because these tunnels are the lowest ones for altitude, thus we can expect the highest interaction between percolate and mineral phases. The values of pH measured on field are lower than the values showed in the past literature and it can be motivated by the influence of rainy season.

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The Mongolian/Slovak Project

ESTABLISH THE GEO-DATABASE ON ECOLOGICAL HEALTH OF THE MILITARY SITES

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Military cooperation between the Soviet Union and Mongolia was long-lasting, particularly in terms of the Mongolian army's Soviet-supported founding and training, which began as early as 1970. After departure of the Soviet Army (SA), most of the original Soviet military buildings were removed between 1986 and 1992, and the areas containing them were either completely abandoned or are only partially used by the Mongolian Armed Forces today. It is estimated that 10% of the areas were reassigned to civil use, 30% to use by the Mongolian Armed Forces and 60% were demolished or abandoned. In 1996 the Ministry of Environment and Green Development of Mongolia, in cooperation with the country's Ministry of Defense, began to investigate the negative impacts of the SA's activities in these military areas, revealing significant environmental damage. In 2000 Mongolian experts conducted a more in-depth study of the former SA sites in the Gobi region, which uncovered major environmental damage and contamination while also recommending ways to mitigate and eliminate it. It is estimated that an area of roughly 2000 km^2 is threatened by hazardous substances, with the most urgent contamination in the regions of Gobisumber, Uvurkhangai, Bulgan, Orkhon and Dornogobi. These findings were also confirmed by the most recent study in 2010.

THE SLOVAK REPUBLIC AS A PARTNER

As the Mongolian government aims to put some of the other former Soviet military areas to civil use, it is essential to begin the process of revitalising them, though this entails a long list of necessary measures. The Ministry of Environment and Green Development of Mongolia, the Ministry of Defense of Mongolia and specialist organisations, represented by the Institute of Geoecology and the Environmental Information Center, thus decided to apply for financial and technical support from NATO's Science for Peace and Security Programme. NATO proposed closer cooperation with the Slovak Republic (SR), a NATO member with experience addressing contamination resulting from the Soviet Army's activities. The Slovak Environmental Agency (SEA) was designated as the contact organisation for the purposes of the cooperation.

THE MONGOLIAN/SLOVAK PROJECT AND ITS OBJECTIVES

The chief objective of the Mongolian/Slovak project **ESTABLISHING A GEODATABASE ON THE ECOLOGICAL HEALTH OF MILITARY SITES** is to address the need for a geodatabase of military sites in Mongolia with an emphasis on the activities of the Soviet Army with information on negative environmental impacts in particular affected areas.

Four basic objectives have been established for the project:
1. Familiarise Mongolian experts with international methodological practice when determining the state of the environment in areas used for military purposes.
2. Create a geodatabase for the evaluation of the ecological situation resulting from the SA's activities between 1970 and 1990.

3. Determine and evaluate the level of contamination in areas damaged by military activities.
4. Prepare an official strategy for the decontamination and rehabilitation of areas damaged by the SA's activities in Mongolia.

THE MONGOLIAN PARTNERS' FIRST STUDY TOUR AND TRAINING

In November 2013, the project's first study tour was undertaken by a Mongolian delegation consisting of specialists from the Mongolian Ministry of Defense, the Institute of Geoecology and the Environmental Information Center in Ulan Bator. The goal of the study tour was to introduce Mongolian experts to the techniques applied in the investigation, remediation and monitoring of contaminated areas, a field in which the Slovak Republic has extensive experience, given that the Soviet Army's activities there between 1968 and 1991 left behind widespread pollution, particularly contamination of groundwater by petrochemicals and chlorinated hydrocarbons. There are a total of 87 such potentially contaminated sites in 18 localities, 15 of which have been determined as seriously contaminated. There was a clear need for significant financial investment in further investigation and particularly remediation, which began to be implemented in 1993 and continues intermittently today (in areas such as Lešť, Sliač and Komárno).

As mentioned above, after the similarly damaged areas of Mongolia have been remediated and potentially reclaimed, the Mongolian government aims to use them for civil purposes. Because Slovakia has several areas originally used by the Soviet and Slovak armies that are now used for civil purposes, these were presented to the Mongolian delegation. One such area is the Old and New Fortress in Komárno, which was used first by the Soviet Army and subsequently by the Slovak Army. The Mongolian delegation was familiarised with the rich history of this remarkable area, as well as the original sources of the contamination and the types of investigation, monitoring and remediation work that have been implemented there.

The second locality visited was Lešť, which continues to be used for military purposes. As the largest area significantly contaminated by the SA's activities, Lešť served as an appropriate example of efforts to address contamination.

After a site has been investigated, the samples taken need to be analysed, and thus the SEA organised a visit to the specialised laboratories of the Soil Science and Conservation Research Institute (SSCRI) in Bratislava and the Regional Centre of the Dionýz Štúr State Geological Institute (DSSGI) in Spišská Nová Ves. The SSCRI staff acquainted their Mongolian partners with the laboratory techniques of assessing soil contamination, though the visitors expressed particular interest in the SSCRI's presentations on remote sensing and the Partial Monitoring System (PMS) – Soil. The regional centre in Spišská Nová Ves was noted for its well-equipped laboratory specialising in the analysis of contaminated groundwater, sediments and soil.

The project's most prominent activities have also included a specialised training of Mongolian partners in Mongolia, led by Slovak experts and held in and around Ulan Bator in June 2014. The Slovak experts prepared a wide range of lectures focused on the methods of addressing contamination resulting from the SA's activities in Slovakia, presenting the process of investigation, remediation and monitoring, as well as the types of remediation appropriate for the elimination of the impacts of contamination in military areas. The lectures also presented systematic procedures for the assessment of health and environmental hazards and the associated international standards and limits. Particular attention was devoted to the methods and techniques used to investigate and monitor military sites. The Slovak experts presented selected inorganic and organic substances that appear in Slovakia as a result of military activities, and they explained their dangerous properties with regard to health and the environment.

The project's training activities have also included fieldwork in Mongolia's Nalaikh military area, which has up to now been limited to a preliminary survey because the Mongolian organisations involved in the project are not yet appropriately equipped for an in-depth investigation. Another deficiency that Mongolian specialist organisations have to address is the insufficiently equipped state laboratories, which are not currently prepared for rigorous analyses involving substances such as petrochemicals, polycyclic aromatic hydrocarbons or chlorinated hydrocarbons.

The project's next key objective is the creation of a geodatabase of military areas, and to this aim lively discussions have been held between Mongolian and Slovak experts on the design and particularly the content of the upcoming database.

THE NEXT STEPS—A SECOND STUDY TOUR

A second study tour of Slovakia for Mongolian partners is being prepared for April 2015 as a follow-up to the previous one in November 2013. Its goal is to acquaint Mongolian specialists with various types of remediation currently being implemented on sites damaged by the SA's activities in Slovakia and to step up consultations on the creation of the geodatabase, which is already underway, using the basic information obtained on 27 military areas in Mongolia.

The most significant outcome of the project Establishing a Geodatabase on the Ecological Health of Military Sites is the preparation of the Strategy for the Elimination of Contamination Resulting from the Activities of the Soviet Army in Mongolia Between 1970 and 1990, an endeavour that will also be part of the planned study tour.When complete, this strategy will be presented to the Mongolian government, among others.

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THERMAL EXPERIENCES IN DENMARK

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KEYWORDS
Remediation, chlorinated solvents, thermal treatment, off gas treatment

BACKGROUND

Denmark has a water supply based almost solely on groundwater. Therefore, a large amount of work has been carried out to find old contaminated sites in order to prioritize clean-up efforts. Many contaminants threaten the groundwater, the most commonly found in the abstraction wells in more urban areas are chlorinated solvents and to a lesser extent different pesticides.

The Danish MCL for the chlorinated solvents are 1 ppb in ground and drinking water or less indicating that very effective means for the remediation are necessary. In Denmark most of the remediation effort, including for chlorinated solvents, has been done by excavation and off site treatment, but in some cases in-situ methods has been shown more feasible and therefor chosen as a remedy strategy. A branch of the remediation techniques that have shown very high efficiencies are different kind of thermal treatment.

Until now approximately 15 full scale or experimental clean up using thermal techniques has been carried out in Denmark. Some experiences and lesson learned from the remedies are presented in the following.

Heating techniques & methods

The three most common used techniques for soil heating has been direct steam injection (SI), thermal conductive heating (TCH) and electrical resistance heating (ERH). Radiofrequency heating (RFH) has been tested on a pilot scale in a few applications also.

SI and injection of steam/air mixtures requires a certain permeability in the soil that is treated. Applicability are limited to fine sand and above in grain size in order to obtain energy injection rates that are high enough to cover a site with a limited number of wells. The contaminants treated has mostly been chlorinated solvents like tetrachloroethylene and trichloroethylene as well as minor amounts of heating oil. The maximum achievable temperature in the soil using steam as the energy source is around the boiling point of water, 100° C at atmospheric pressure. Below the groundwater, slightly higher temperatures are possible.

TCH has mostly been used in lower permeability settings like clayey till contaminated with chlorinated solvents. Most of the remedies has used electrical immersive heaters as the energy source although a couple has used gas driven heater elements as the heating source. The gas driven heaters (GTR) has an advantage compared to the electrical in that way the internal flame in the heaters can destruct removed vapors by direct combustion in some cases. Temperature possible to obtain in-situ depends a lot on the ability to control any influx of water. If water is present temperatures around the boiling point of water normally is the goal temperature. For removal of higher boiling compounds like heating oil, tars, denser chlorinated pesticides, PCBs etc. goal temperatures of up to 350-400° C are possible to obtain with the method, but that requires a complete dry-out of the soil.

Electrical resistive heating (ERH) has been applied at a couple of sites in full scale. The technique utilizes the fact that the soil itself is a resistor. When a voltage potential is applied between a set of electrodes a current is introduced and energy absorbed in the soil according to Ohms law. Since most of the electrical system throughout the world is based on three-phase alternating current, the electrode configuration normally consists of a multiple of triangles with an electrode in each corner. In order to get the best contact between the surrounding soil and the electrodes granulated graphite is usually used as the material between electrode and soil. In addition, vertical spacing between electrodes is used in order to be able to control energy distribution through different layers. The field strength, and hence energy deposition is biggest near the electrodes. Normally water is added to the electrodes in order to avoid complete drying of the soil volume near the electrodes and thereby further increasing resistivity and energy deposition in close proximity to the electrodes.

In almost all the Danish cases except for the GTR remedies the treatment system has comprised of a cooling system, a water and gas phase separation and a following treatment of the vapor and water phase in GAC.

Separation of any free phase liquid is done before GAC filtering the liquid phase. Groundwater pumping and soil vapor extraction are used to gain pneumatic and hydraulic control at any treated site.

RESULTS

Remedy efficiency

In general, all the remedies have had high efficiencies. The remedy objectives have varied from means of flux reduction to fixed concentration values in the soil matrix based on soil sampling.

The largest steam injection case was carried out in 2006 in the southern part of Denmark removing approximately two tons of PCE and TCE from 20.000 m³ of soil down to 15 m below the groundwater table (20 mbg). The mass flux was reduced within the first year from almost 100 kg/year to appr. 4 kg/year. In 2011 sampling was repeated and the mass flux was further reduced to less than 0,5 kg/year corresponding to a mass flux reduction of more than 99%.

An example from a recent remedy of TCE at a former industrial site in clayey till (volume 7.000 m³ above ground water) resulted in a removal rate of more than 99 % as seen in Figure 1.
The technique was TCH. Most control samples taken after the heating period has non-detect values i.e. below 0.01 mg/kg.

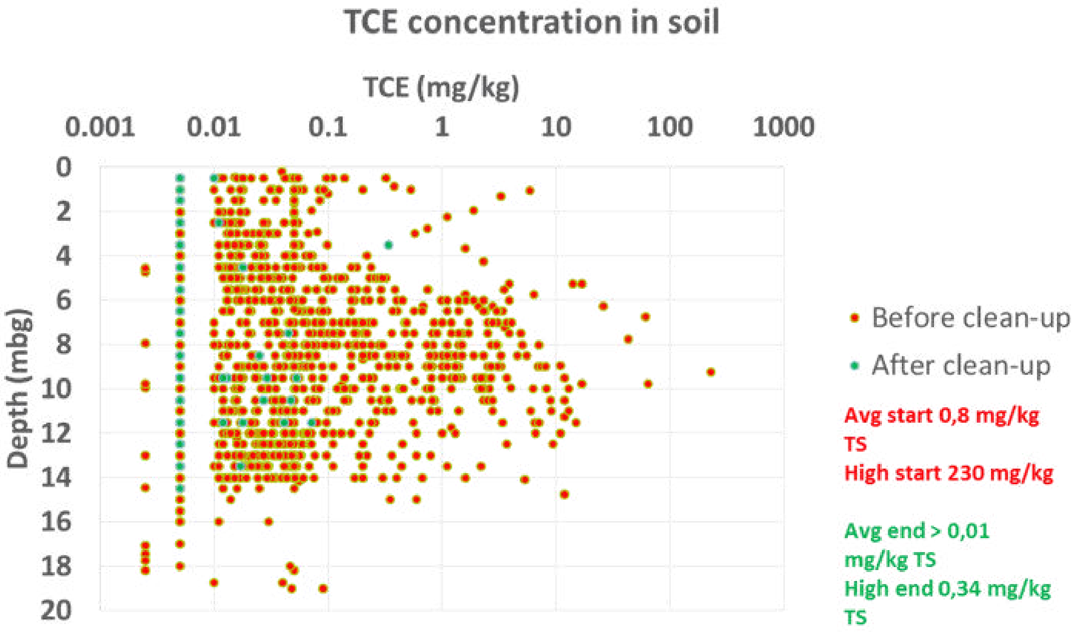

Fig. 1. Concentration in soil before and after clean-up. Detection limit was 0.01 mg/kg DW.

Other thermal conductive heating cases shows similar result when the chlorinated solvents has been the target. There are results from one case where heating oil was the target. I that case the end concentration was below 25 mg TPH/kg DW in the control samples.

Figure 2 show results from an electrical resistivity heating remedy. The removal rate is a bit lower than for the conductive heating cases. The operator probably didn't run the heating period for a period long enough to ensure that the remediation goals was obtained in the complete volume. Another lesson learned from the ERH cases is that even minor changes in spacing and placement between electrodes lead to a costly process of revising the project with respect to running parameters. Compared to TCH the ERH seems less flexible in the installation phase. Often placement of wells etc. needs to be rescheduled due to obstacles in the soil or other complications, which shows more expensive with ERH than TCH. The advantage observed in the cases using ERH is that the power consumption is a bit lower than for TCH.

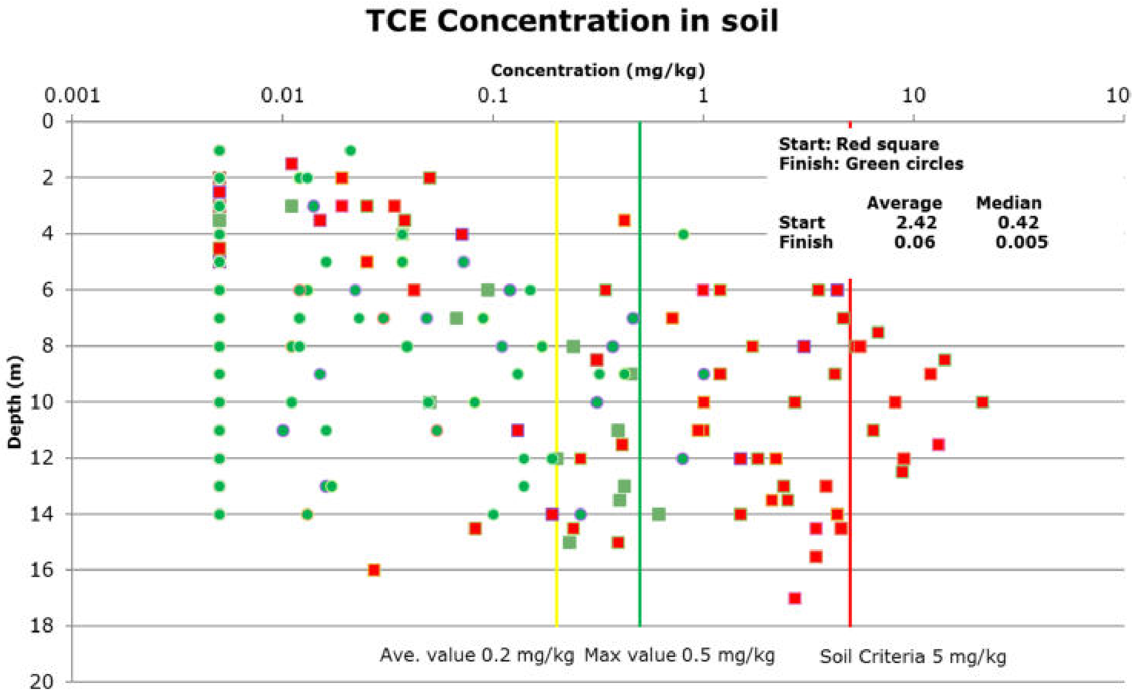

Fig. 2. Results from an ERH remedy in clayey soil

Geotechnical aspects

One of the factors that always get discussed are the geotechnical implication of heating the soil, drying out the soil more or less depending on the target temperature and clean-up goals.

In Denmark a lot of the soil is pre-consolidated due to ice that covered most of the country 10.000 years ago and before. That type of soil typically is clayey till and/or sand with low organic carbon content. The experiences using thermal techniques in these soil types are that settlement (and raising) are very limited. Minor cracks in the masonry has been observed, but generally damage is cosmetically.

As a prevention a geotechnical assessment is always part of a thermal project, looking for organic soils like peat etc. and measuring soil strength parameters before applying any heat. Organic rich sediments are known to settle during heating and oxidizing so if organic rich soil are present special considerations needs to be taken.

Economy

The price tag on thermal treatment has been rather high, due to a limited number of vendors but prices are being moderated at the moment in Denmark. Tab. shows size of remedy, heating method, target contaminants and some short results together with the unit price for the treatment.

CONCLUSION

During almost 20 years, thermal remediation has been used in Denmark. The three most common methods has been direct steam injection (SI), thermal conductive heating (TCH) and electrical resistance heating (ERH). All three methods have shown strong result with respect to removal rates. SI has been applied successfully in a number of more permeable sites whereas TCH and ERH has been applied at low permeable sites. The size of the sites has varied from a few hundred m^3 up to 50000 m^3. Almost all the cases have had chlorinated solvents as the target removing from less than 100 kg up to 3500 kg depending on the size of the site and the source strength. On most of the sites, some or the entire contaminant source zone has been below buildings and in many cases at greater depths (down to approximately 20 mbg). Economy ranges between 100 up to 1100 Euros/m^3 treated soil. There is a tendency that larger sites have lower unit costs and that SI is cheaper than the other methods. SI is not patented while there are vendors with patents on both TCH and ERH.

Tab. 1. Economy in a subsample of different thermal remedies as a function of size and target contaminants.

Case	Year	Volume (m^3)	Method	Target Contaminant	Results	Price (Euro/m^3)
Brüel og Kjær	1997	4000	Steam	PCE/TCE	1.500 kg removed	?
Hedehusene	1999	50000	Steam	PCE/TCE	800 kg removed, 95 % removal rate	100
Østerbro Ålborg	2000	1200	Steam	PCE/white spirit	800 kg removed, Dissolved concentrations reduced > 99%	280
Cliprens, Rødekro	2004	9600	Steam	PCE	2000 kg removed, Mass flux reduced > 99%	270
Knullen	2008	2500	Steam/TCH	PCE	3500 kg removed, removal rate > 99%	1070
Skuldelev	2008	1500	TCH	PCE	400 kg removed	1100
Reerslev	2009	11100	TCH	PCE	2500 kg removed, removal rate > 99%	430
Albagrunden	2011			PCE	?	?
Vadsbyvej	2010	1000	TCH	PCE/TCE/TCA	200 kg removed	?
Innovationsgaragen	2013	-	TCH, gas driven	PCE	Demo project, In flame destruction of PCE	-
Innovationsgaragen	2013	-	Radio Frequency Heating	-	Demo project. Obtaining more than 100°C in soil	-
Bregnerødvej	2013	2250	ERH	TCE	35 kg removed Average soil below 0,02 mg/kg	650
Pilehøj Vænge	2014	7000	TCH	TCE	130 kg removed, removal rate > 99%	200
Marstrandsvej	2014	150?	TCH, gas driven	Heating oil, TPH	<10 kg left in soil, concentration below 25 mg TPH/kg	?

UTILIZATION OF AOPS FOR DEGRADATION OF EMERGING CONTAMINANTS AND REACTIVE DYES

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KEYWORDS
AOPs, toxicity screening, reactive dye, NSAID

ABSTRACT

In the last decades advanced oxidation processes (AOPs) appear to be a promising alternative for the degradation of persistent pollutants. Therefore, conventional wastewater treatment technologies are being reinforced by AOPs as a prior or post treatment. These processes are based on the formation of very reactive oxidative species such as hydroxyl radical (•OH), which can mineralize organic pollutants 0. The degradation efficiently of generally used AOPs depend on hydrogen peroxide, UV light, Fenton reaction, catalyst (Fe, TiO_2) [Calvosa et al. 1991] or a different combinations of these factors. Special sort of AOPs is application of electrical discharges for water decontamination. In this study two types of AOPs were applied for degradation of reactive azo dye and emerging contaminants as anti-inflammatory non steroidal drug (NSAID): electrochemical and dielectric barrier discharge (DBD) treatment.Degradation efficiency was followed by HPLC-DAD, and some of the degradation products were identified by LC-MS (TOF). After the each treatment toxicity screening of degradation products was performed by two bioassays: bioluminescent bacterial and brine shrimp test.

MATERIALS AND METHODS

Degradation efficiency of reactive blue (RB 52, 60 mg/L) azo dye and ibuprofen (60 mg/L) was calculated by equation: $\eta = (Po\text{-}Pt/Po) * 100$, where η was the degradation efficiency (%); Pt (mAU*min) was the peak area of the azo dye or ibuprofen concentration at a given energy/time of tretment; Po was the peak area of initial azo dye or ibuprofen concentration. Electrolytic systems consisted of undivided electrochemical cell where the cathode was Zr, Pd or C, while the anode was always Fisher Pt electrode and the power source was DC power supply PS3010 (0-32 V DC, 0-10 A) E – HQTM. The solution of ibuprofen and azo dye was treated at pH 3 or 7. The non-thermal plasma reactor with DBD was used for degradation of ibuprofen. The HPLC - Dionex UltiMate 3000 chromatograph with photodiode array detection (DAD) was used with C8 Hypersil Gold aQ (150mm x 3mm, 3μm) column and the LC Agilent Technologies 1200 Series chromatograph (with DAD) coupled with Agilent Technologies 6210 TOF - mass spectrometer. Ecotoxicology tests were performed using *Artemia salina,* cysts - DAJANA PET, Czech Republic (Persoone & Wells, 1987) and *Vibrio fischeri* NRRL B-11177, ISO 11348-3.

RESULTS AND DISCUSSION

The degradation efficiency of reactive blue azo dye RB52 after applying electrochemical degradation technique was the highest at pH value of 3. Therefore, the optimal value of voltage for azo dye decolorization was studied for all reaction systems (Pt-Pd, Pt-Zr or Pt-C) by applying various values of voltage: 4.5, 6 or 12 V at pH 3.
Electrochemical system of Pt-Pd acchieved the fastes decolorization of RB52 reaching 92% after only 50 min of tretment time at pH 3 and voltage of 6V. In the electrochemical Pt-C electrochemical system the degradation eficiency of 92 % was acchieved after 100 min at pH value of 3 and voltage value of 12V.
The most efficient electrochemical system for decolorization of RB52 was Pt-Zr system, where the acchieved decolorization was 95 % after 90 min tretmant time at pH 3 and voltage value of 4.5 V.
Degradation of azo dye at optimal conditions for degradation in every electrochemical system (Pt-Pd, Pt-Zr or Pt-C) was monitored on HPLC-DAD and the peak of RB52 had t_r= 5.32 min.The chromatograms were recorded

after the treatment of RB52 solution in all three systems at the maximum percentage of decolorization. The most pronounced difference in the degradation products was observed in Pt-Pd system, where at the retention time of about 3 min there was an absence of product, which appears in other systems (Pt-Zr and Pt-C). The peak area of RB52 has been reduced in all treated solutions. The ecotoxicological tests on *A.salina* and *V.fischeri* have shown great sensitivity to degradation products of RB52 solution after the treatment. The *V.fischeri* was the more sensitive model.

The highest degradation percentage of ibuprofen in the electrochemical treatment was achieved during the treatment with Pt-Pd system (98%). In other two treatments degradation of ibuprofen was 88.5% for Pt-Zr and 82% for Pt-C treatment.

During the non-thermal plasma with DBD treatment 9 degradation products were identified: four aromatic and five aliphatic carboxylic acids. The degradation efficiency of ibuprofen after 15 min of treatment in non-thermal plasma with DBD was 85%.

Using the LC-MS (TOF), hydroxylated ibuprofen molecules were detected among the first degradation products. In the case of Pt – Pd system (after 30 min) only aromatic structures were detected. The mortality of *A. salina* was not detected for ibuprofen solution treated with NTP- DBD and less than 30% was detected at 100% (v/v) of a sample treated with electrochemical system Pt-Pd.

The reported ibuprofen's EC_{50}/LC_{50} value for *V. fischeri* ranges from 12.1 to 19.1 mg/L (Ferré et al. 2001). After the NTP-DBD treatment no toxic effect was recorded. However, after the exposure to ibuprofen solution treated with Pt-Pd, the EC_{50}/LC_{50} values were not determined, rather just the inhibition percentage which ranged from 35% to 45 %.The test validity criteria - survival in the negative control and reference toxicant tests were within the range of acceptable values.

CONCLUSION

The efficiency of DBD treatment of ibuprofen after the 15 min was 85% and accompanied by opening of the aromatic ring. After the Pt-Pd treatment aromatic structure was preserved. *A.salina* showed no significant toxic effect when exposed to all post treatment solutions of ibuprofen, however it was more sensitive to solutions of RB52 treated in electrochemical cell. *V.fischeri* toxicity test has shown greater sensitivity to Pt-Pd treatment in comparison to *A.salina* for both degradation methods.

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THE UCB SITE IS POLLUTED IN ACID TAR

Claudia Neculau

ABSTRACT

Initially occupied in part by coke ovens and installations for the recovery of coke residue, the site has grown significantly in the late 1920s with the development of a large chemical plant.

The preliminary characterization and feasibility studies held on site, have shown that due to the past industrial activities during more than one century, soil and underground waters in the majority of these zones are very polluted in polycyclic aromatic hydrocarbons, monocyclic aromatic hydrocarbons, mineral oils, heavy metals and acid tar.

The rehabilitation works started in 2009.

Several stages of works were thus realized previously on this site.

The first stage consisted of deconstruction of buildings and remaining infrastructures of the former factory. The other four stages were intended for the soil rehabilitation on various parts of the former factory. The sixth stage of rehabilitation consists of the treatment of the contaminated soil resulting of tar pourings.

The main problem of the current stage of the rehabilitation works lies in the management of acid tar, and more precisely, fighting against the bad smells and the dispersal of the pollution. Consequently, specific measures were undertaken to protect the local residents and the workers, and to control permanently the air quality and the direction of the prevailing winds, and many others.

Several experimental tests were realized on site before the starting up of the works, in view to find the optimal method to neutralize the acid tar (PH from 1 to 3) and to validate the management systems of the volatile emissions.

The presentation will focus on the rehabilitation strategies and the innovative methods implemented by SPAQuE during the rehabilitation works.

NO NET LAND TAKE BY 2050 – REALITY OR SCIENCE FICTION FOR MUNICIPALITIES

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KEYWORDS

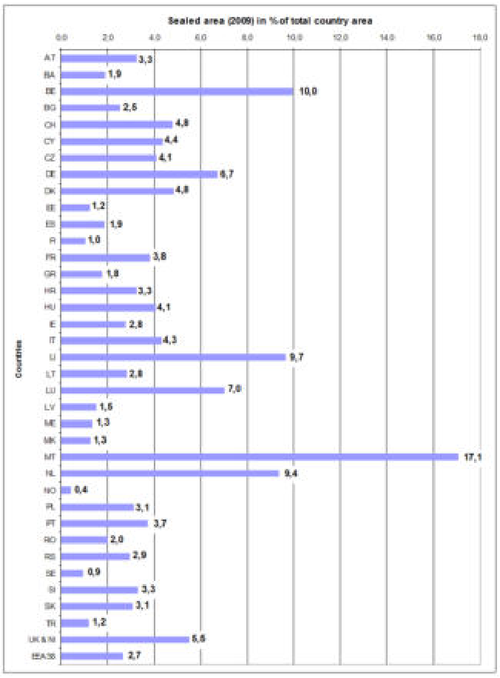
Soil functions, soil properties, soil management, urban soil, brownfields, heavy metals, soil pollution, sustainable spatial planning

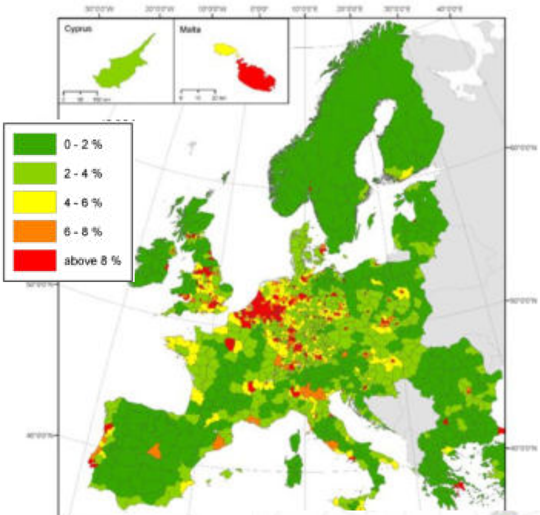
ABSTRACT

Soil is defined as the top layer of the earth's crust. It is fundament of habitats, agriculture and all human activities. Is fundamental to all land uses. In context of history of human civilisation is non-renewable natural resource. It is formed by mineral particles, organic matter, water, air and living organisms. This mixture of substances, known as soil, provides a very wide range of ecosystem functions – not only production of food and biomass, it offers biological habitats and gene pools for below and above ground biodiversity, can clean water which replenish the aquifers, exchange nutrients, store carbon, transform pollutants. Soils can also be source of raw materials (peat, clay, gravel,...), protect archaeological treasures and help regulating the microclimate through the landscape. Finally yet importantly, soils provide support for socioeconomic structures.

Soil sealing and land take affect all of these functions as no functions; no ecosystem services that soil provides can no longer be executed.

Data collection across Europe shows that *land take is worrying*. More than 100,000 hectares of mainly agricultural land are taken annually for urbanisation purposes in the 27 EU Member States. The European Union is supporting urban development as a key factor for economic growth, while at the same time the natural resources as a basis for life ought to be protected. Decisions what, where and how much land should be taken and sealed are often made too automatically in a planning and decision making process.





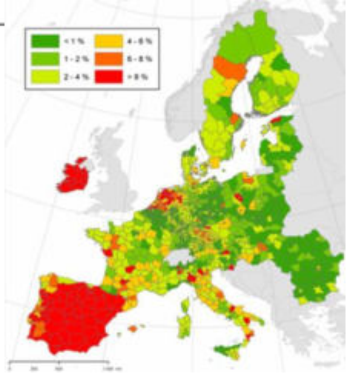


Fig. 1&2. Sealed area in % per country and NUTS3
Fig. 3. Rise of sealed area per NUTS3 regions in years 2000-2006

Above shown figures show significant soil sealing changes in a short period. Part can be explained by low sealing rate of region and high urbanisation and infrastructure growth.

However, does sustainability play a role when deciding where and how much soil will be taken for new urbanised area? Do the planners and stakeholders take into account soil quality? Is inner instead Greenfield land take weighted and evaluated in different aspects?

In many cases and based on experiences from i.e. Central Europe project URBAN SMS unfortunately not. Nevertheless, in EU we do have light at the end of the tunnel. European Commission has recognised that problem and has considered loss of soil through sealing in the Soil Thematic Strategy (COM (2006) 231) in 2006. More recent actions are Roadmap to a Resource Efficient Europe (COM (2011) 571) which proposes that by 2020 the rate of land take (i.e. loss of agricultural, semi-natural or natural land for the development of urban areas and infrastructure) is on track with an aim to achieve no net land take by 2050.

Can we expect obstacles with soil protection policies implementation on EU, state and municipal level?

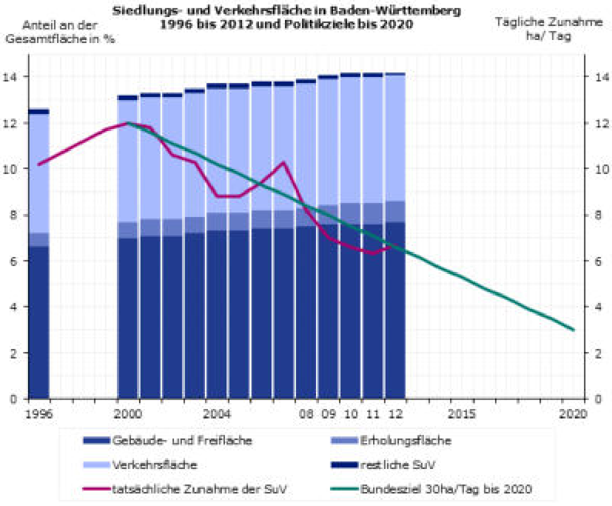


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Fig. 4. Settlement and traffic sealed area in Baden-Wuerttemberg 1996 to 2012 and policy goal until 2020

For sure yes. The first sign is withdrawal of the Soil Framework Directive proposal in May 2014, but fortunately, Seventh Environment Action Plan recognises soil degradation as a serious challenge. In addition, some main EU countries do have specific legislation on soil protection. I would name Germany as a good example and its federal state Baden-Wuerttemberg that has made political statement to achieve no net land take. On Figture 4 we can see some results of such political decision. But where politicians do not recognise importance of unsealed soil the conflict of (long term) soil protection versus (short term) economic development is or will be faced. Therefore, management strategy and experiences are thus required for practical implementation of soil protection strategies at regional and local level.

Besides that environmental legislation, dealing with brownfield remediation should be standardised on EU level. Currently legislation often does not Recognise importance of soil type and land use when setting trigger values of soil contamination.

For example, in Germany Federal Soil Protection Act allows use of soil for industrial purposes up to, i.e. 60 mg/kg Cd, while in Slovenia national Decree sets limit trigger value at 12 mg/kg Cd in soil. In some border cases that can leads to successful remediation processes and avoiding new land take while in other can lead to too high remediation expenses for investors and new land take on Greenfield.

What can we conclude from above written facts?

Europe has had different historical development of industry and settlement models thus high variations in % sealed area are fact which results in higher sealing rates in countries with delayed economical and traffic development that mostly have also lower general sealing rates. In terms of soil, degradation and contamination are not such high derogations due to similar industrial procedures (not in terms of aerial degradation). For future wellbeing of our non-renewable natural resource, *soil*, some actions are required. Perhaps the first ones are management strategies and experiences for the practical implementation of soil protection at regional and local level. Combined with awareness raising activities and a permanent and unceasing commitment on the European, national and local level, these actions may lead to the goal of better protection of soil resources in Europe and final goal No net land take by 2050.

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